ALLOYS OF IRON RESEARCH, MONOGRAPH SERIES

FRANK T. SISCO, EDITOR

THE ALLOYS OF IRON AND COPPER

ALLOYS OF IRON RESEARCH

Monograph Series

THE ALLOYS OF IRON AND MOLYBDENUM *by* J. L. Gregg

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THE ALLOYS OF IRON AND COPPER

BY

J. L. GREGG

Research Engineer, Bethlehem Steel Company

AND

B. N. DANILOFF

Graduate Student, Carnegie Institute of Technology

This monograph has been prepared at Battelle Memorial Institute as a part of the Institute's contribution to Alloys of Iron Research

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ALLOYS OF IRON RESEARCH

MONOGRAPH SERIES

THESE monographs are a concise but comprehensive critical summary of research on ferrous alloys as reported in the technical literature of the world. They contain a discussion of all available data on binary and higher ferrous alloy systems, and on the effect of the alloying elements on carbon steel and on simple and complex alloy steels and special alloy cast irons. They provide a reliable foundation for further research and in one volume supply to the practical metallurgist, steel worker, foundryman, and engineer the essential information now scattered through more than two thousand journals and textbooks in many languages.

The authors are responsible for selection and evaluation of the data, for arrangement of subject matter, and for style of presentation. Each book, however, has been reviewed in manuscript by men especially qualified to criticize all statements. Indebtedness for this cooperation is recognized in the Acknowledgments. Finally, each manuscript has been reviewed and approved for publication by the Iron Alloys Committee.

The Committee expresses its appreciation to *The Engineering Foundation*, the *iron and steel, automotive and other industries of the United States and the American Iron and Steel Institute, Battelle Memorial Institute, The American Foundrymen's Association*, and *National Bureau of Standards*, for financial support, which made the laborious review of the world's literature possible; and to the libraries, engineering societies, and the technical press in the United States, Canada, England, Germany, France, Italy, Sweden, Japan, and Czechoslovakia, for cooperation in making available inaccessible reports and in permitting the use of published data.

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PREFACE

This is the fourth volume of the monograph series. The first volume, "The Alloys of Iron and Molybdenum," was published in 1932, the second, "The Alloys of Iron and Silicon," in 1933, and the third, "The Alloys of Iron and Tungsten," in 1934. The aims of this and other monographs are described on a preceding page and in the Preface to the first volume of the series.

Although published abstracts have been used in locating original literature and for eliminating duplicate and secondary articles, the original sources of the important data have been studied, especially abstracted or translated, and the articles themselves consulted repeatedly in the preparation of the monograph. There were located 634 pertinent articles, of which abstracts were made. Of these, 399 appear in the selected bibliography at the end of this monograph. Reference numbers are used liberally in the text in order that the source of the published data and statements may be readily found. Although reference is made to several patents, no systematic study of the patent literature was made.

As in the three other monographs of the series, properties of industrial materials are given in units of the English system. In the sections dealing with equilibrium diagrams only centigrade temperatures are given, but in other sections both Fahrenheit and centigrade temperatures are shown. The property variously reported in the literature as elastic limit, proportional limit, or yield point has been termed *yield strength*, unless it was determined in accordance with the definitions of elastic limit or proportional limit proposed by the American Society for Testing Materials (*Proceedings*, v. 31, part 1, 1931, pp. 602–604).

J. L. GREGG.
B. N. DANILOFF.

BETHLEHEM, PA.,
October, 1934.

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The preparation of the monograph was undertaken by Battelle Memorial Institute as a part of its contribution to Alloys of Iron Research, and the work was written while the authors were members of the staff of the Institute. As was the case with the other monographs prepared at Battelle Memorial Institute, the laborious searching of the literature and its preliminary abstracting in order to select the articles important enough for detailed study were done by Miss Lois F. McCombs, Bibliographer, while Miss Thelma Reinberg, Librarian, was helpful in many phases of the work. The help of other members of the staff of the Institute was freely given, and the authors are particularly grateful for the helpful comments obtained from Mr. C. E. Williams, Director, Dr. H. W. Gillett, Metallurgist, and Dr. C. H. Lorig, Metallurgist.

Through the courtesy of the Anaconda Copper Mining Co., the American Brass Co., and the Copper and Brass Research Association many heretofore unpublished data on alloys of iron and copper were made available for inclusion in the monograph. Some of these data were obtained at the research laboratory of the American Brass Co. by Dr. Cyril Stanley Smith and Mr. Earl W. Palmer; others were obtained at the Battelle Memorial Institute, in work sponsored by the Copper and Brass Research Association. Dr. H. Foster Bain, Director, was kind enough to put at the authors' disposal all results obtained for the Association at Battelle Memorial Institute. The investigations at the Institute were carried out under the direction of Dr. C. H. Lorig, who, together with others working with him, including Mr. A. W. MacLaren and Mr. D. E. Krause, were very obliging in locating and interpreting data on copper steels and irons.

Other data that had not been published in the technical literature were made available through the courtesy of Mr. A. Finlayson of the Pacific Car and Foundry Co., Mr. D. Zuege of the Sivyer Steel Casting Co., and officers of the Bethlehem Steel Co.

Preliminary drafts or selected portions of the monograph were read by members of the Iron Alloys Committee and by those listed below, and revisions were made in line with their uniformly useful comments:

H. Foster Bain	Copper and Brass Research Association
C. H. Desch	National Physical Laboratory, Teddington, England
U. R. Evans	Cambridge University, England
A. Finlayson	Pacific Car and Foundry Co.
J. Johnston	Research Laboratory, United States Steel Corporation
V. V. Kendall	National Tube Co.
V. N. Krivobok	Carnegie Institute of Technology
J. H. Nead	Inland Steel Co.
E. W. Palmer	American Brass Co.
W. G. Schneider	Copper and Brass Research Association
E. H. Schulz	Forschungs-Institut der Vereinigte Stahlwerke A.-G., Dortmund, Germany
C. S. Smith	American Brass Co.
S. C. Spalding	American Brass Co.
F. N. Speller	National Tube Co.

J. L. GREGG.
B. N. DANILOFF.

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October, 1934.

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THE ALLOYS OF IRON AND COPPER

CHAPTER I

INTRODUCTION

The Metal Copper—Copper in Iron-base Alloys

Copper was one of the first, if not the first, of the metals smelted by man. In antiquity it was used as the crude metal or alloyed with tin or zinc. Vast quantities of the commercially pure metal and of brasses and bronzes are used today. The copper consumed in the United States in 1931 amounted to nearly one million tons.

Iron-base alloys containing copper do not date back far; on the contrary, copper steel is of quite recent origin. Compared with its other uses, the amount of copper used in ferrous products is still small. Bain and Schneider[343] estimated that at the present time about 2000 tons of copper are used annually in iron and steel in this country.* On the basis of present tonnage copper is hardly to be classed as a major member of the group of metals used in alloy steel. But on the basis of potentialities, as yet not very widely appreciated except in the one instance of 0.25 per cent copper steel for corrosion resistance, copper deserves a more prominent place. This potential importance results from the facts that copper is among the cheapest alloying elements and that only relatively small amounts are required to confer desirable properties. Both economics and technology thus point toward more extensive utilization of copper as an intentionally added alloying element in ferrous alloys.

A. THE METAL COPPER

Before considering alloys of iron and copper, it may be well to pay some attention to the occurrence, characteristics, and

* In a private communication, E. H. Schulz of Vereinigte Stahlwerke, A.-G., wrote that in Germany the yearly use of copper in steel amounts to approximately 500 tons.

properties of copper itself. Obviously, a detailed consideration of these subjects is beyond the scope of this book, and only very brief summaries are given below.

1. Copper Production.—According to the *Minerals Yearbook*,[356] the average annual world production of new copper for the years 1925 to 1929 was 1,761,500 short tons. During this period the average annual production from the mines in this country was 885,800 short tons. In 1932, the world production of new copper was only 990,000 short tons and the production from mines in this country only 240,000 short tons.

Rawles[370] wrote that "about one-half of the world's copper industry is located in the United States and the next most important, though distinctly subordinate, regions are Chile, Canada, and South-Central Africa."

2. Commercial Copper.—Most of the copper used in commerce is of the variety known as "tough-pitch." Its distinguishing characteristic is its oxygen content, which is in the neighborhood of 0.04 per cent; oxide particles in this material are readily visible under the microscope. Tough-pitch copper may or may not contain significant amounts of impurities other than oxygen. In the United States there are three principal grades of copper now recognized—electrolytic copper, Lake copper, and casting copper. Electrolytic copper and prime Lake copper are sufficiently pure to have a high electric conductivity. Other Lake coppers and casting coppers may contain impurities which reduce their conductivity to a fraction of that of electrolytic and prime Lake copper.

Electrolytic copper is marketed either as cathodes or after melting the cathodes and casting into such shapes as wire bars, ingots, and cakes. The great bulk of the electrolytic copper is marketed in the fire-refined condition. Except for the few ounces per ton of silver, prime Lake copper is of a purity comparable with electrolytic copper, as is shown by the analyses in Table 1 from the publication compiled by Bain and Schneider.[343]

In addition to tough-pitch copper, deoxidized coppers are commercially available. These materials may or may not contain appreciable quantities of the deoxidizer and other impurities. The deoxidizer most frequently used is phosphorus, but copper deoxidized with this element under conditions that are not precisely controlled may have a relatively low conductivity owing to the retention of traces of phosphorus in the metal and possibly

TABLE 1.—ANALYSES OF AMERICAN COPPERS*

Element	Average for electrolytic refined,† per cent	Electrolytic‡ (melted cathodes), per cent	Prime Lake,§ per cent	Natural arsenical Lake,§ per cent	Casting,‡ per cent	
Copper + silver	99.9565	99.9548	99.9500	99.9100	99.45	
Copper	99.9550	99.9530	99.9200	99.8800	99.44	99.50
Silver	0.0015	0.0018	0.0300	0.0300	0.01	
Lead	0.0010	0.0010	0.000	0.0000		0.05
Bismuth	0.0001	0.0000	0.0000	0.0000	0.01	
Arsenic	0.0008	0.0000	0.0020	0.0400	0.02	
Antimony	0.0007	0.0009	0.0000	0.0000	0.05	
Selenium + tellurium	0.0014	0.0026	0.0000	0.000		
Iron	0.0018	0.0038	0.0020	0.0020	0.38	0.06
Nickel	0.0010	0.0028	0.0015	0.0015		0.15
Zinc		0.0000	0.0000	0.0000		
Sulphur	0.0017	0.0026	0.0015	0.0015	0.002	
Oxygen (by difference)	0.035	0.0315	0.0430	0.0450		Trace
Tin						0.18
Total	100.000	100.000	100.000	100.000	99.912	99.94

* Bain and Schneider.(343)

† Analysis given by Skowronski of Raritan Copper Works.

‡ Analysis by American Brass Company.

§ Analysis by Calumet and Hecla Consolidated Copper Company. If specified, arsenical Lake copper may be obtained with from 0.06 to 0.50 per cent arsenic.

to the absorption of impurities from the refractory container in which the copper was melted.

In all high-conductivity copper the impurity content is so low that impurities introduced by the copper into iron-copper alloys need not cause great concern.

3. Properties of Copper.—Properties of copper as compiled by C. S. Smith of the American Brass Company and published in the 1933 *National Metals Handbook* are given in Table 2.

TABLE 2.—PROPERTIES OF COPPER*

Atomic weight	63.57
Atomic volume	7.11
Crystal structure at 20°C	Face-centered cubic
Length of unit cube, Å	3.6078
Density at 20°C., g. per cu. cm	8.94
Density at 1083°C. (solid), g. per cu. cm	8.32

* *National Metals Handbook*, 1933 ed.

TABLE 2.—PROPERTIES OF COPPER.—(*Continued*)

Density at 1083°C. (liquid), g. per cu. cm	7.93
Melting point, °C	1083.0
Melting point, °F	1981.4
Boiling point, °C	2325
Boiling point, °F	4217
Specific heat, cal. per g. per °C., at 25°C	0.0919
Latent heat of fusion, cal. per g	50.46
Linear coefficient of expansion, per °C., at 25°C., $\times 10^6$	16.47
Electric resistivity at 20°C., microhms per cu. cm	1.682
Electric conductivity at 20°C., megmho per cu. cm	0.594
Thermal conductivity at 20°C., cal. per sq. cm. per cm. per sec. per °C	0.923
Magnetic susceptibility, $\times 10^6$	−0.085
Electrochemical equivalent, Cu″, mg. per coulomb	0.32940
Electrochemical equivalent, Cu′, mg. per coulomb	0.65880
Viscosity at 1145°C., c.g.s. units	0.0341
Surface tension, 1150°C., dynes per cm	1104
Reflectivity, λ = 6500 Å, per cent	80
Reflectivity, λ = 4500 Å, per cent	37

B. IRON-BASE ALLOYS

Although copper was intentionally added to wrought iron (as an experiment) several hundred years ago, very little satisfactory information regarding the influence of copper in ferrous products was obtained prior to the present century.

4. Copper as an Adventitious Element.—Iron ores usually contain small amounts of copper, and because oxides of copper are unstable in the presence of metallic iron the copper in ores enters the iron rather than the slag. The copper content of iron or steel made from copper-bearing ores has been found to be as high as 0.3 or 0.4 per cent, and many of the early ferrous products contained enough copper to be classified at the present time as copper-bearing materials. There is little evidence that adventitious copper had an influence, either good or bad, on the properties of iron or steel made in the early days; at least there is little evidence that its influence was detectable by the test and inspection methods of those days. Writers have claimed that the long life of some of the early products could be ascribed to the presence of a small amount of copper, but this is difficult to substantiate.

5. Early Observations Regarding the Influence of Copper.—The early studies of copper in ferrous products were confined mainly to whether copper was soluble in iron, the influence of

copper on the behavior of wrought iron during manufacture, and whether copper produced red-shortness.

In 1901, Stead quite definitely proved that copper dissolved in iron, although as late as 1906 Pfeiffer, on the basis of actual experimental work, concluded that even in the liquid state copper did not actually dissolve in iron but was highly dispersed as a suspension in the iron.

Lipin, in 1895, proved that as much as 1 per cent copper in wrought iron did not interfere with its manufacture and that there was no reason to fear a few tenths of 1 per cent of copper in wrought iron.

Early work did not determine whether copper produced red-shortness in low-carbon iron and steels. Even recent observations have been in conflict, but it is now known that copper does not produce red-shortness, and that it is possible to cast homogeneous carbon-free ingots of all compositions. However, a layer of metallic copper, formed just below the oxide scale, frequently tends to produce surface cracking upon deformation at temperatures above the melting point of copper, and copper steels may appear to be red-short, even though they are not in the strict sense of the term.

6. The Iron-copper Diagram.—The first equilibrium diagram, a creditable first approximation, was constructed by Sahmen in 1908. Extensive work of Ruer and associates between 1913 and 1917 resulted in the construction of a diagram of fair accuracy. Since the appearance of Ruer's diagram no one has carefully investigated the entire series of alloys, but several workers have studied portions of the diagram and suggested modifications. As a result, a reasonable diagram has been outlined, but the exact locations of many of the lines are rather uncertain.

7. Modern Studies of Iron-copper Alloys.—The most notable investigations of the properties of alloys relate to corrosion resistance. Extensive long-term exposure tests of copper-bearing steels conducted here, in Germany, and in England quite definitely proved that the addition of as little as 0.2 per cent copper to low-carbon wrought materials appreciably increased the resistance to atmospheric corrosion.

More recently, investigators here and abroad have shown that iron-rich alloys can be hardened by inducing precipitation and that such a treatment may find commercial application. The alloys are somewhat unusual in that they need not be quenched

in order to produce a supersaturated solution, so as to be in condition for the precipitation treatment. Air-cooled as well as quenched samples can, therefore, be hardened by reheating to a temperature in the neighborhood of 500°C. (930°F.).

8. Use of Copper in Iron and Steel.—The so-called copper-bearing steel, containing about 0.20 per cent copper, is well known and is widely used for structural purposes and sheet on account of its resistance to atmospheric corrosion. A few copper-alloy steels, notably copper-chromium, copper-manganese, and copper-molybdenum, are used rather widely in Europe. Extensive work in Germany has shown that copper-chromium steels, containing approximately 0.6 per cent copper and 0.3 per cent chromium, have a high yield strength in the as-rolled condition, and that as a result they are an economical structural material. No other copper-containing steel has wide application.

A very limited quantity of nickel-copper steels is now used, and some of the stainless alloys contain a few per cent of copper. A limited quantity of steel containing 1 per cent copper is employed where a certain degree of resistance to chemical attack is required, as for oil-well equipment. As much as 7 per cent copper is contained in recently introduced austenitic nickel-chromium cast irons. Copper is now used to a limited extent in American malleable iron and gray iron. Recent work has indicated that copper-bearing malleable iron has good properties and responds readily to the malleableizing treatment.

While the precipitation-hardenable steels containing copper give promise of finding useful applications, they have not yet had real commercial use, except in the case of the cast steels developed by Kinnear.[291]

CHAPTER II

CONSTITUTION OF IRON-COPPER ALLOYS

Early Work on Solubility of Iron and Copper—Suggested Diagrams—The Probable Equilibrium Diagram—Authors' Summary

The iron-copper diagram is of decided interest for theoretical and practical reasons, because it exhibits certain features that have not been found in diagrams for other metals. There is a miscibility gap in the liquid state, but the field of immiscibility does not intersect the solidus and the gap is widened as temperature increases. There is some indication that alloys in the neighborhood of 9 per cent copper form a homogeneous solid solution at high temperatures and partially liquefy on cooling. As in many other systems, the components in the solid state form limited series of solid solutions; the solubility of one component in the other decreases with decreasing temperature. No compounds are formed; the only solid phases formed are solutions of one metal in the other.

A. EARLY WORK ON SOLUBILITY OF COPPER IN IRON

Study of the literature reveals that attempts to alloy copper with iron or steel may be traced as far back as one hundred years,[2] or even more.[1] Early experiments on alloying copper with pure iron are interesting from the historical point of view but are of little significance in the study of the constitution of iron-copper alloys, because no account has been taken of the influence of various impurities that might be present and because of the unreliability of the early methods for identifying the constituents of the alloys.

9. Alloying Copper with Iron.—As reported by Percy,[11] Rinmann, in 1782, made an alloy of 5 parts iron and 1 part copper.* "The alloy was hard and tough. Its fracture was white

* In commenting on the first draft of this monograph C. H. Desch of the National Physical Laboratory wrote: "It might be better to refer to the original book, the German edition of which I have. The title is *Geschichte des Eisens*, German translation by C. J. B. Karsten, 1815, and the section

with black points, presenting no sign of copper, but here and there upon the surface it had a copper-like skin."

Another experiment, also reported by Percy, was made by Karsten, who stated that iron (it is not clear from the report whether cast iron or low-carbon iron) can take up only a certain, probably a very small, percentage of copper.

Mushet,[4] in 1835, made a series of experiments to determine the practicability of alloying iron with copper. He melted wrought iron with 5, 10, and 20 per cent of its weight of copper and noted the extent to which the copper was dissolved; then he melted cast iron with similar proportions of copper. By examining the alloys thus obtained he found that, when the copper content exceeded 5 per cent, cast iron showed a greater tendency than steel to form liquid layers. Mushet attributed this difference to the influence of carbon and concluded that "copper unites with iron in proportion as the latter is free from carbon."

From the results of a series of experiments made in Percy's laboratory[11] it would appear that iron and copper could be alloyed in all proportions. Alloys were made from iron wire and electrolytic copper to contain about 17, 20, 50, 58, and 80 per cent iron. All of them melted well; the first three appeared to form homogeneous liquids.

Bauerman[18] stated that iron may be melted in all proportions with copper but that no compound is formed unless a third element is present.

Summarizing the results of various investigators, Howe[22] declared that iron and copper probably unite in all proportions. Alloys of iron with small proportions of copper, and of copper with small proportions of iron, appear to be homogeneous whether molten or solid, but with nearly equal amounts of copper and iron two liquids are formed.

As reported by Stead,[39] Greenwood stated that the direct alloying of iron and copper is attained with difficulty, but an apparently homogeneous alloy can be obtained by the simultaneous reduction of the oxides of iron and copper.

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describing a large number of experiments on the alloying of copper with steel begins on page 70 of volume II. Rinmann considered that the opinion that copper makes iron red-short is incorrect, and his experiments confirmed it. His translator, Karsten, disputes this and believes in the evil effect of copper. I doubt whether Karsten made experiments of his own. In his text-book, a copy of which I also have, he appears only to be quoting Rinmann."

In his brief review of the work of previous investigators, Pfeiffer[47] mentioned the work of Riche who observed the separation of iron-copper melts into two layers, one containing four times as much iron as copper. He assumed that by maintaining the melts in the liquid state for a sufficiently long time a complete separation into two layers can be obtained and concluded that the liquid solubility of copper in iron is practically nil.

10. Investigations on the Intersolubility of Iron and Copper.—No exact quantitative data on the extent of solid solubility of copper in iron and of iron in copper appeared in the literature until the results of Stead's[39] investigation were published in 1901. In making his alloys, Stead used copper containing 0.27 per cent of total impurities and No. 5 British Association Standard steel containing 0.035 per cent carbon, 0.32 per cent manganese, with other impurities low and amounting, together with carbon and manganese, to 0.46 per cent. The alloys were melted and allowed to solidify very slowly. As the result of an extensive series of experiments Stead concluded that:

1. Copper and iron alloy in every proportion by direct fusion, and in none of the alloys is there any tendency for the metals to separate into two conjugate layers.
2. The complete series of alloys may be classed into three distinct sections.
   a. Alloys with from traces to 2.73 per cent iron.
   b. Alloys with between 2.73 and 92 per cent iron.
   c. Alloys containing between traces and 8 per cent of copper.

Stead considered that all these mixtures may be called "true alloys," being free from globules and knots of iron and copper, although it was very difficult to alloy iron with a little copper without admitting some silicon or oxide of iron. Alloys of class *a*, with less than 2.73 per cent iron, are homogeneous and consist of only one metallographic constituent—a solid solution of iron in copper. Alloys of class *c* containing from traces to about 8 per cent copper are homogeneous solid solutions of copper in iron. When the amount of iron in copper exceeds 2.73 per cent, or the amount of copper in iron exceeds 8.0 per cent, the alloys are no longer homogeneous and are found to consist of two phases, which are two solid solutions—one rich in iron and the other rich in copper. From his observations of the polished sections of the alloys he concluded that on solidification of the alloys of class *b* the first part to separate from solution is rich in iron, and that, as the solidification proceeds gradually, the liquid phase becomes

richer in copper; also that, as the crystals grow, more and more copper separates out with the iron until the last portion solidifies with a maximum proportion of copper.

Contrary to Stead, Pfeiffer[47] came to the conclusion that in the solid state copper dissolves in iron only to a very slight extent, possibly not more than 0.5 per cent, and that in the liquid state copper is not dissolved in the iron but is held in suspension.

B. SUGGESTED DIAGRAMS

The early investigations reviewed above have thrown some light on the constitution of the iron-copper alloys; however, the results reported by various investigators were conflicting and did not supply sufficient information to form even an approximate picture of the iron-copper system.

11. The Diagram of Sahmen.—The first diagram for the system iron-copper was worked out by Sahmen[52] in 1908. The melts were made in an electric furnace under an atmosphere of nitrogen using electrolytic copper and steel contain ng 0.07 per cent carbon, 0.06 per cent silicon, 0.10 per cent manganese, 0.019 per cent sulphur, 0.015 per cent copper, and 0.01 per cent phosphorus.

According to the diagram of Sahmen, shown in Fig. 1, copper and iron dissolve in all proportions in the liquid state; in the solid state copper is soluble in gamma iron to the extent of about 3.5 per cent, and copper dissolves about 2.75 per cent iron; between 3.5 and 97.25 per cent copper the alloys consist of two solid solutions, one rich in iron and the other rich in copper. Copper was thought to be insoluble in alpha iron. No account was taken of delta iron.

The liquidus line was determined by means of cooling curves. The temperature of the beginning of solidification of the alloys falls gradually as the copper is increased to 30 per cent; between 30 and 70 per cent it remains almost constant at about 1430°C. On further increase in copper content it falls rapidly to 1100°C. (97.25 per cent copper) and finally falls to the melting point of copper.

The solidus, starting from the melting point of iron, falls rapidly to 1100°C. at the concentration of about 3.5 per cent copper, corresponding to the solubility limit of copper in gamma iron, then remains at constant temperature toward point *b* on the copper side of the diagram representing the final stage of

the solidification of the copper-rich solid solutions in the heterogeneous alloys. From *b* it falls to the melting point of pure copper. The temperature of the horizontal part of the solidus was determined by Heycock and Neville[29] as 10°C. above the melting point of copper, which places it at 1093°C.

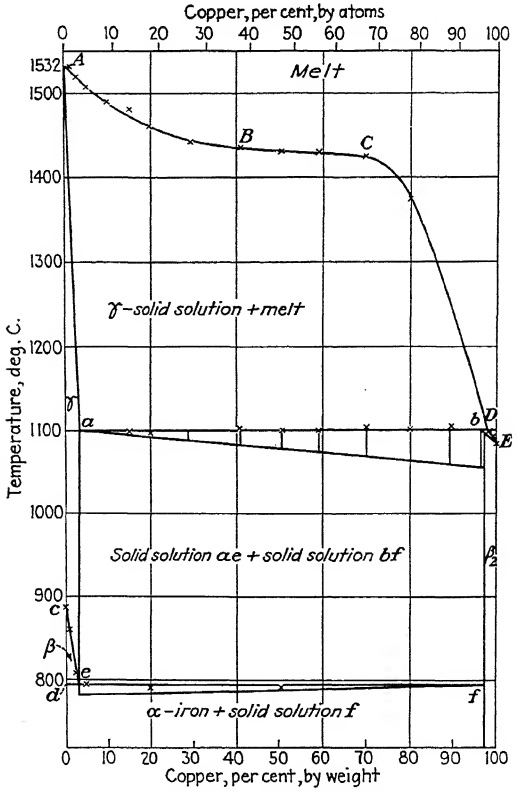


FIG. 1.—Iron-copper equilibrium diagram according to *Sahmen*.[52]

The line representing the solubility of copper in gamma iron drops sharply to the eutectoid point *e* at 791°C., and the solubility curve of iron in copper was drawn vertical from the peritectic temperature (1100°C.) to room temperature, according to the belief then held that in the solid state the solubility of iron in copper remains constant.

The gamma-alpha transformation determined by thermal analysis was found to be lowered by the addition of copper in amounts up to 3.5 per cent and then remain constant at 791°C. The temperature of the magnetic transformation (795°C. as reported by Sahmen) was found to be independent of the copper content, but the copper-rich solid solution was found to be non-magnetic. Since the difference between the temperatures of the magnetic transformation and the eutectoid transformation is within the limits of experimental error, the diagram is drawn as if the points *e* and *d* were at the same temperature. Below line *def* the alloys consist of alpha iron and the solid solution whose composition is represented by point *f* (2.75 per cent iron).

The disagreement between Sahmen and Pfeiffer regarding the solubility of iron and copper in the liquid state led Oberhoffer[54] to a further investigation of the system. From his study he concluded that the metals are not completely soluble in the liquid state; the existence of the almost horizontal part of the liquidus in Sahmen's diagram suggested the gap in liquid solubility.

12. The Iron-copper Diagram of Ruer.—Disagreement between Sahmen and Pfeiffer and Oberhoffer with respect to the mutual solubility of iron and copper in the liquid state, and some of the inconsistencies and questionable points of Sahmen's diagram, led Ruer and Fick[73] and later Ruer and Goerens[85] to new investigations of the system.

A complete diagram was published by Ruer and Fick in 1913. Since, however, some parts of the diagram, particularly the liquid-solubility curves, still were not definitely determined, Ruer and Goerens continued the study, and in 1917 they published their corrected diagram. This diagram is reproduced in Fig. 2. In the first investigation electrolytic copper and iron containing 0.08 per cent carbon and 0.12 per cent other impurities were used; in the second investigation the iron used was of higher purity, the total amount of impurities being stated as 0.042 per cent or less. The alloys were melted in an atmosphere of nitrogen.

The essential characteristics of the system according to the diagram are briefly as follows: Iron and copper are only partially soluble in both the liquid and the solid state. Between 23.8 and 85 per cent copper two immiscible liquids are formed and separate into two layers. Dissimilar to what happens in other known metallic systems, the mutual liquid solubility decreases with rising temperature. The melting point of iron is lowered by the addi-

tion of copper. At room temperature the solubility of copper in iron was placed as 1 per cent and the solubility of iron in copper as 2 per cent.

The diagram represented in Fig. 2 will be described in some detail. In contradiction to Sahmen, iron and copper were found to be only partially miscible in the liquid state, and the solid solubility of copper in iron at high temperatures was found to be much greater than previously determined by Sahmen. A new

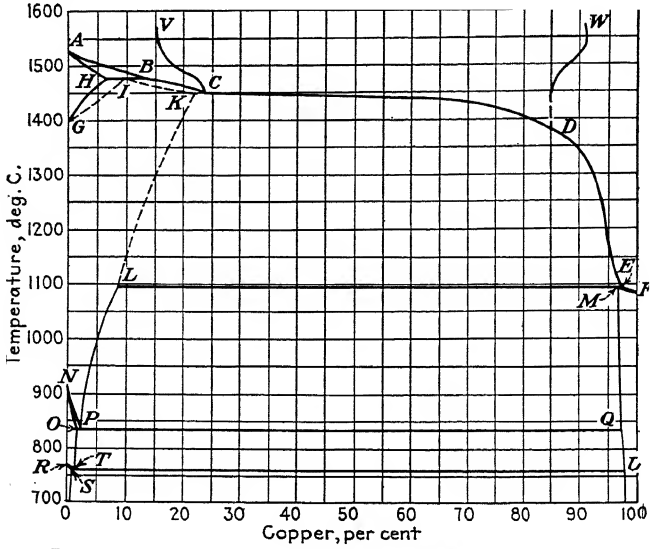


FIG. 2.—Iron-copper equilibrium diagram according to *Ruer and Goerer*

field of a solid solution based on delta iron was also introduced by Ruer and his associates.

The melting point of iron is lowered by addition of copper to 1477°C. at 13 per cent and to 1450°C. at 23.8 per cent copper. On further addition of copper, from 23.8 to 85 per cent, the liquidus drops very slowly, the total drop within this range of concentration being only 75°C. From point *D* it drops very rapidly to *E* at 1094°C. and 97.5 per cent copper, and then to the melting point of copper at *F*.

The solubility in the molten state was found to decrease with the rise of temperature; the amount of iron dissolved in copper and the amount of copper dissolved in iron at various temperatures are shown in the following table.

Temperature, °C.	Percentage of iron in copper-rich layer	Percentage of copper in iron-rich layer
1445	15.0	23.8
1471	14.5	23.1
1490	12.9	19.9
1539	8.7	15.7
1572	9.4	15.3

These values were determined by holding the molten alloys at the desired temperatures from 10 to 30 min. to allow sufficient time for separation into layers; the alloys were then quenched and examined microscopically, and the layers analyzed for iron and copper. Lines *CV* and *DW* were claimed to represent the true equilibrium conditions for the alloys.

The portions of the solidus represented by lines *HB* and *LE* were determined by thermal analysis. Point *M*, determined by microscopic study of the structure, is placed at 97 per cent copper. The horizontal line *LME* lies 10°C. above the melting point of copper, *i.e.*, at 1094°C. Point *L*, representing the limit of solid solubility of copper in gamma iron at this temperature, was determined thermally and microscopically as 8.5 per cent copper. From *L* the solidus runs to point *K*, which was not determined experimentally but was put at approximately 22 per cent copper, representing the extent of the solid solubility of copper in gamma iron at 1450°C. Point *I*, representing the composition of the phase formed peritectically at 1477°C., was also estimated. It will be observed that if this diagram is correct alloys with 8.5 to 22 per cent copper, solid above line *LK*, will partially liquefy on cooling through the range of temperatures between *LK* and *LM* and will freeze at *LM*.

The temperature of the delta-gamma transformation of iron is raised by the addition of copper from *G* at 1401°C. for pure iron, to *H* at 1477°C. and 6.5 per cent copper, which is the intersection of line *GH* with the horizontal *HIB* (the peritectic transformation involving delta solid solution, gamma solid solution, and melt, of compositions *H*, *I*, and *B* respectively). At point *B* there is a break in the liquidus line; the alloys solidifying along *AB* separate out the primary crystals of the delta solid solution, and alloys solidifying along *BC* give rise directly to crystals of gamma solid solution. The completion of the delta-gamma transformation represented by the broken line *GI* was not determined experi-

mentally but was believed to represent the true equilibrium conditions. The details of this part of the diagram determined by Ruer and Klesper[76] by means of thermal analysis are shown in Fig. 3.

Copper has much the same effect as carbon on the transformation temperatures of iron; hence the iron-rich part of the diagram is of the same type as that of the system iron-carbon.

The values obtained by thermal analysis for the liquidus, the solidus, and the beginning of the delta-gamma transformation are given in Table 3 from the studies of Ruer and Goerens.[85]

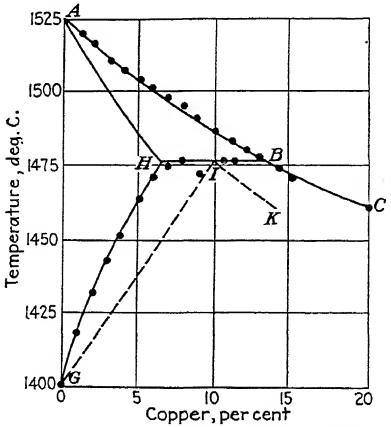


FIG. 3.—Delta region of the iron-copper diagram. (*Ruer and Klesper.*[76])

In the peritectic reaction at 1094°C. gamma solid solution, copper-rich melt, and copper-rich solid solution of compositions *L*, *E*, and *M* respectively are involved. This temperature was determined by thermal analysis (Table 3). The alloys with over 97.5 per cent copper solidify as homogeneous solid solutions of iron in copper. Solubility decreases very slightly with falling temperature, being about 2 per cent at 759°C. and below; according to Ruer and Goerens, the alloys containing over 98 per cent copper remain unchanged on cooling down to room temperatures.

At 906°C. gamma iron changes into alpha iron. Addition of 2.3 per cent copper lowers the transformation to 833°C., and on further increase in copper content it remains practically constant until at point *Q* (97.5 per cent copper) the transformation is no longer observed, the copper-rich solid solution remaining unchanged down to room temperatures.

TABLE 3.—RESULTS OF THERMAL ANALYSIS FOR LIQUIDUS, SOLIDUS, AND DELTA-GAMMA TRANSFORMATION OF IRON-COPPER ALLOYS*

Composition, per cent		Temperature, °C.			Composition, per cent		Temperature, °C.		
Fe	Cu	Beginning of solidification	Beginning of delta-gamma transformation on cooling	End of solidification	Fe	Cu	Beginning of solidification	Beginning of delta-gamma transformation on cooling	End of solidification
100	0	1528	1401		75	25	1450	.....	1094
99	1	1520	1418		70	30	1448	.....	1095
98	2	1516	1431		65	35	1445		
97	3	1511	1442		60	40	1444	.....	1094
96	4	1508	1453		50	50	1441	.....	1095
95	5	1505	1463		45	55	1440		
94	6	1502	1471		40	60	1438	.....	1093
93	7	1498	1475		35	65	1435		
92	8	1496	1477		30	70	1430	.....	1095
91	9	1492	1473		25	75	1419		
90	10	1487	1477	1093	20	80	1407	.....	1095
89	11	1484	1477	1094	15	85	1375	.....	1094
88	12	1482			10	90	1344	.....	1094
87	13	1479			5	95	1182	.....	1094
86	14	1474			3	97	1111	.....	1094
85	15	1472	....	1095	2.5	97.5	1094		
80	20	1461	....	1094	2	98	1091		
77	23	1451	....	1094	0	100	1084		

* Ruer ‡

The temperatures of the gamma-alpha transformation obtained by thermal analysis are shown in Table 4. As may be seen, the critical points obtained by cooling and by heating show considerable lag. It was also found that the temperature of the transformation depends on the temperature from which the specimens are cooled.(85) The higher the temperature, the lower the transformation. This is shown below for a 4 per cent copper alloy:

	Gamma-alpha transformation on cooling, °C.
Alloy as cast	730
Cooled, then heated at 1000°C	798
Cooled, then heated at 910°C	809
Cooled, then heated at 888°C	815
Cooled, then heated at 863°C	817
Cooled, then heated at 853°C	817
Cooled, then heated at 848°C. (30 min.)	818

TABLE 4.—THE GAMMA-ALPHA TRANSFORMATION IN IRON-COPPER ALLOYS*

Composition, per cent		Transformation on cooling		Transformation on heating		Gamma-alpha transformation temperature, mean between upper on heating and lower on cooling, °C.
Fe	Cu	Temperature range, °C.	Mean temperature, °C.	Temperature range, °C.	Mean temperature, °C.	
100	0	905 to 906	906	906 to 907	906	906
99	1	856 to 858	857	866 to 868	867	862
98.5	1.5	848 to 851	850	860 to 863	861	855
98	2	838 to 841	840	841 to 843	842	841
97.7	2.3	823 to 826	825	840 to 843	841	833
97.5	2.5	818 to 823	821	845 to 848	846	833
97.2	2.8	823 to 826	825	840 to 843	841	833
97	3	818 to 823	821	845 to 848	846	833
96	4	818 to 823	821	843 to 848	845	833
94	6	821 to 823	822	845 to 848	846	834
92	8	818 to 823	821	845 to 848	846	833
91	9	818 to 821	820	848 to 851	849	834
90	10	818 to 823	821	845 to 848	846	833
89	11	818 to 821	820	848 to 851	849	834
85	15	818 to 821	820	851 to 853	852	835
80	20	818 to 821	820	851 to 853	852	835
77	23	817 to 820	819	851 to 853	852	835
75	25	817 to 820	819	851 to 853	852	835
70	30	818 to 821	820	851 to 853	852	835
60	40	817 to 820	819	851 to 853	852	835
50	50	817 to 820	819	851 to 853	852	835
40	60	817 to 820	819	851 to 853	852	835
30	70	816 to 819	818	851 to 853	852	834
20	80	816 to 819	818	851 to 853	852	834
10	90	816 to 818	817	851 to 853	852	834
5	95	No longer observed				

* Ruer and Goerens.[85]

The temperature of the magnetic transformation of pure iron (768°C.) was found to be lowered to 759°C. by the addition of 1 per cent copper and to remain constant up to 98 per cent copper as shown by line *TU*. Above 98 per cent copper, in the region of copper-rich solid solutions, the magnetic transformation was no longer observed. The magnetic transformation was found to be practically reversible, *i.e.*, to occur at the same temperature on heating as on cooling. The heat effect of the magnetic transformation is weak and decreases with the increase in copper content. Specimens with 95 and 97 per cent copper were tested magnetically. In the former the change in magnetic permeability was noted at 762 to 756°C. on cooling, and at 756 to 762°C. on

heating; in the latter a very weak effect was noted at 759°C. both on heating and on cooling.

From electric-conductivity measurements the solubility of copper in alpha iron at all temperatures below 759°C. was estimated as about 1 per cent.

13. Inconsistency of Ruer and Goerens' Diagram with the Phase Rule.—The existence of the region of immiscibility in the liquid state as indicated on Ruer and Goerens' diagram is not consistent with the fact that the liquidus is in no part horizontal. Since between *C* and *D* two liquid phases are found in equilibrium with a crystalline phase, the temperature of *CD*, at constant pressure, according to the phase rule, must remain constant. This is in contradiction to the experimental results which indicate a temperature drop of 75°C. between the points *C* and *D*. There is one degree of freedom too many, and the system suggests the behavior of a three-component system. Ruer[85,191] attempted to explain this inconsistency by an assumption that in view of the imperfect stability of the system during solidification a certain crystalline entity (*Molekülart, Kristallart*) of a very slow rate of formation or disintegration is formed, which plays the rôle of a third component.

14. Discussion of Ruer's Diagram and Later Work.—The inconsistency of Ruer's diagram with the phase rule and certain other points aroused considerable discussion by other investigators, which resulted in some modification of the diagram and eventually led to the construction of a diagram consistent with many of the experimental data and the requirements of the phase rule.

Commenting on the discrepancies between the results of Sahmen and of Ruer and his collaborators, Ostermann[158] suggested that the region of immiscibility of iron and copper in the molten state exists, but that the liquid-solubility curves gradually approach each other with falling temperature and come together at about 20°C. above the liquidus, thus forming a closed loop inside of which two conjugate solutions exist. If the melt is heated to a temperature inside the loop so that it separates into two layers, cooling through the temperature drop of some 20°C. at the usual rate may not allow sufficient time for the melt to attain the new equilibrium, and it would solidify in two layers. Ostermann also brought forth another argument in support of his assumption, *viz.*, that if a small amount of carbon is added to

the melt the separation into layers is always effected; according to Guertler, a small amount of carbon is sufficient to depress the solubility line so that it touches the liquidus, and the higher the carbon content the wider apart are the points at which the two curves intersect, or, in other words, the less the mutual solubility of the two metals. The effect of carbon in decreasing the solubility of iron and copper in the liquid state had already been noticed by Stead[39] and by Mushet.[4]

In support of Ostermann's hypothesis, Müller[188] commented that a closed immiscibility loop, although it has never been observed in binary metallic systems, occurs in non-metals and especially in mixtures of organic substances with water. The "International Critical Tables" (vol. III, pp. 389–396, 417) give several binary systems which exhibit the lower critical point on the liquid-solubility curves. Among these are:

System	Lower transformation temperature, °C.	Upper transformation temperature, °C.
Water—nicotine	60.8	208
Water—ethylene-glycol monoisobutyl ester	24.5	150.4
Glycerol-*m*-toluidine	6.7	120.5

In order to determine whether or not carbon-free alloys had a miscibility gap in the liquid state, Müller prepared several alloys of equal parts of electrolytic iron and electrolytic copper and held the melts at different temperatures; to insure attainment of the equilibrium condition he maintained the given temperatures for 15 to 45 min. The alloy heated at 1600°C. was found to have separated into two layers. At 1530°C. separation was not so pronounced; at 1480°C. a perfectly uniform structure throughout the alloy was obtained. Figures 4, 5, and 6 illustrate these structures. As the result of these experiments, Müller placed the lower critical temperature at 1500°C., as shown in Fig. 7.

Ruer[191] was not convinced by Müller's experiments and maintained that the existence of the closed immiscibility loop is impossible. The interpretation of Müller and Ostermann appears the more probable and has gained favor with other investigators. Thus Reuleaux,[190] having examined critically the investigations of Sahmen, Ruer and Fick, and Ruer and Goerens, and checked

some of their points experimentally, came to the conclusion that a miscibility gap does exist in the liquid state, but that it closes before freezing temperatures are reached. Benedicks[194] plotted

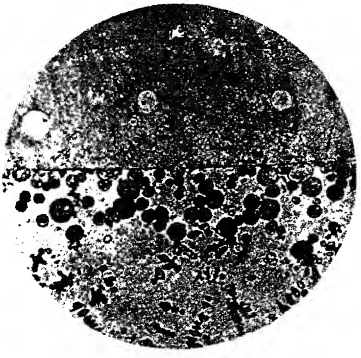


FIG. 4.—Alloy with 50 per cent iron, 50 per cent copper, and 0.03 per cent carbon. Heated to 1600°C. and cooled in the furnace. 50×. (*Müller.*[188])

FIG. 5.—Alloy with 50 per cent iron, 50 per cent copper, and 0.02 per cent carbon. Heated 15 min. at 1530°C. 50×. (*Müller.*[188])

a diagram based on the work of Ruer and Goerens, which complies with both the phase rule and the experimental data (Fig. 8). The liquidus curve as determined by Ruer and Goerens is of the type having an inflection point; the slope of the liquidus at the inflection point is very small; it is obvious, therefore, that a slight shifting of the liquidus curve caused by impurities soluble in iron or in copper is sufficient to bring about the break in the liquid solubility. However, it does not necessarily follow from this that the immiscibility region lies entirely above the liquidus curve. The presence of carbon may lower it gradually, and it is quite possible that the immiscibility loop will partly overlap the liquidus or, in other words, the solubility curve of impure alloys $X\gamma Z$ (Fig. 8) will intersect the liquidus at some points C and D. The position of curve $X\gamma Z$ may change slightly

FIG. 6.—Alloy with 50 per cent iron, 50 per cent copper, and 0.03 per cent

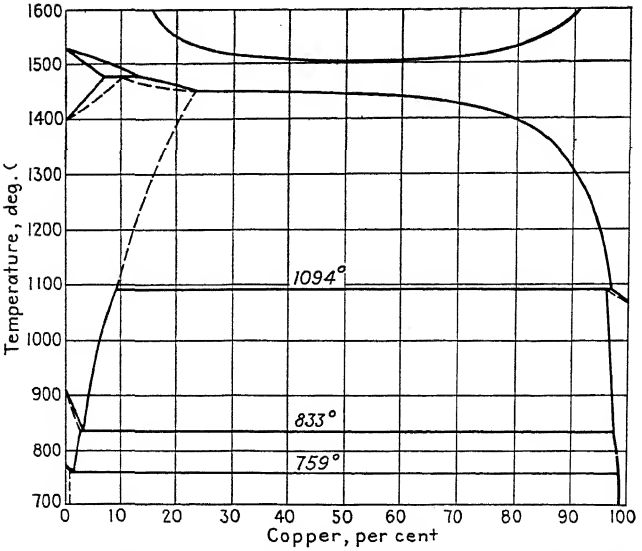


FIG. 7.—Iron-copper equilibrium diagram showing closed loop in the liquid state. (*Müller.*[188])

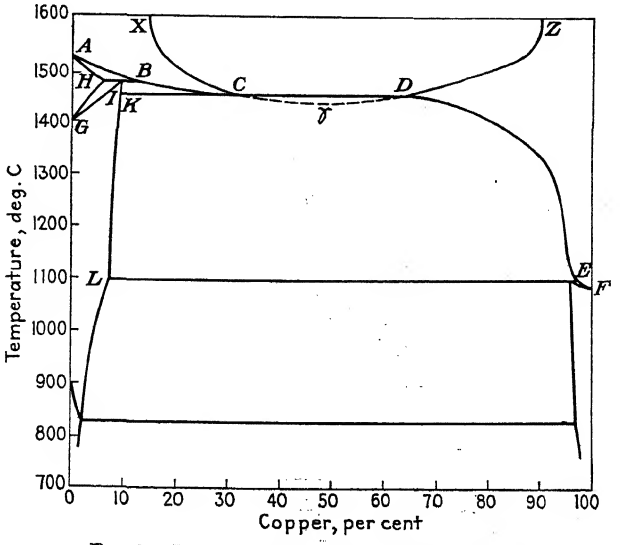


FIG. 8.—Iron-copper diagram of *Benedicks.*[194]

according to the amounts of carbon or other impurities present in the specimens or absorbed during melting. This reasoning of Benedicks seems to have reconciled the two opposing views about the liquid solubility, although, as Benedicks remarked, it did not result in the establishment of a final and conclusive diagram in view of the great accuracy of Ruer and Goerens' experimental determinations.

It should be understood that Benedicks' modification of the iron-copper diagram, as it is shown in Fig. 8, does not represent the true equilibrium conditions of the system but only a special case wherein impurities are present in the alloys. In such a case, with the liquid miscibility gap intersecting the liquidus, line *CD* should be nearly horizontal.

The fact that the liquid solubility decreases with rising temperature is explained by Benedicks as follows: It is well known that the ability of true solids to form solid solutions is the greater the more nearly equal are their atomic dimensions. This may also apply to molten metals. Molten copper at lower temperatures has a smaller atomic volume than iron but a very much greater temperature coefficient. It is possible that with rising temperature the volume difference will increase, and this would possibly tend to decrease the mutual liquid solubility. The behavior of the system at temperatures above 1575°C. was not investigated. The solubilities will possibly increase again at higher temperatures. Such cases are known in many organic systems.

Benedicks also introduced another modification of the diagram by placing point *K* on the line between *I* and *L*, whereas Ruer and Goerens had it nearer to point *C*.

In his modification of the diagram, Guertler (Fig. 9), according to Reuleaux,[190] placed the solid solubility of copper in gamma iron at 12.5 per cent and drew the solubility line *LK* directly to point *I* on the horizontal *HB* (Fig. 2). The slope of the solubility line is the reverse of that of the diagrams by Ruer and others. According to Guertler's diagram, above 1093°C. the solubility of copper in gamma iron would decrease with rising temperature, and this part of the diagram would be similar to the iron-carbon system. Guertler's diagram also eliminates the possibility of the liquation on cooling through the zone between the lines *KL* and *LM* of Ruer's diagram. The liquidus of Guertler's diagram also differs slightly from Ruer's, as may be seen by comparing Figs. 9 and 2.

Ostermann[158] obtained some evidence favoring the views of Ruer and Goerens regarding the increase of solubility of liquid copper in gamma iron with rising temperature and the existence of the liquation zone. In the examination of the structures of

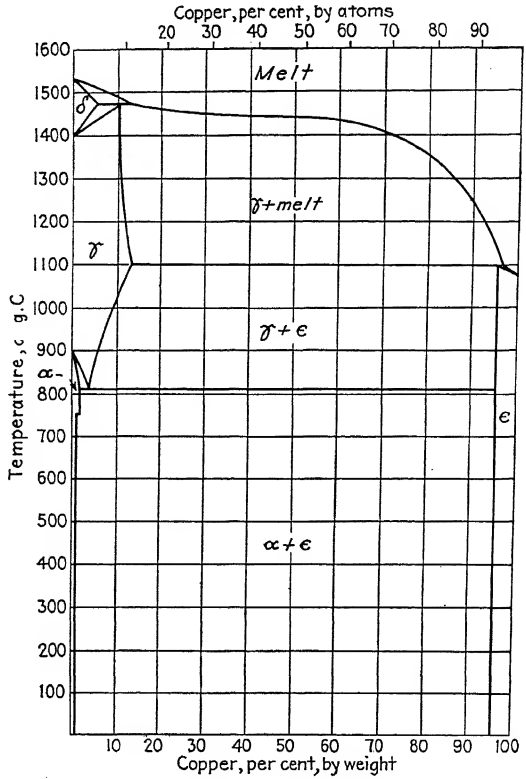


FIG. 9.- -Iron-copper diagram of *Guertler* as given by *Reuleaux*.[190]

iron-copper-manganese alloys he observed a secondary copper-rich constituent. Judging from the nature of this constituent he concluded that the alloy solidified at first as a homogeneous gamma solution, and the copper-rich constituent separated during cooling through the liquation zone as a copper-rich melt. This liquid copper-rich phase on further cooling solidified at the peritectic temperature as a solid solution at the grain boundaries. These observations led Ostermann to believe that the solubility of liquid copper in gamma iron increases with rising temperature and

that the liquation zone actually exists in accordance with the diagram of Ruer and Goerens (Fig. 2).

15. The Diagram below 1094°C.—The extent of the solid solubility of copper in iron below the eutectoid temperature and of the solubility of iron in copper below the solidus were not accurately determined by Ruer and coworkers. From hardness measurements of iron-rich alloys quenched from different tem-

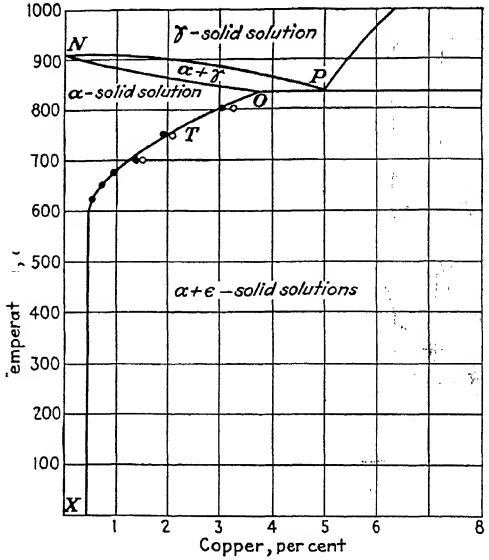


FIG. 10.—Solubility of copper in alpha iron. (*Köster.*)

peratures Isihara[131] concluded that discontinuities in the solubility curve of copper in iron occurred both at the magnetic transformation 750°C. and at the eutectoid temperature. Kussmann, Scharnow, and Messkin,[265] however, determined the hardness and coercive force of iron-rich alloys quenched from various temperatures and found no indication of a discontinuity at the magnetic-transformation temperature. As was to be expected, they observed a discontinuity at the eutectoid temperature, in the neighborhood of 825°C. Neither investigation yielded any data of value on the course of the curve representing the solid solubility of copper in iron.

Precipitation-hardening phenomena of the iron-rich alloys indicate that several per cent of copper are soluble in iron at the

eutectoid temperature, and that the solubility decreases with decreasing temperature. The curve representing the solubility of copper in iron below the eutectoid temperature has not been determined adequately, although the work of Köster and associates, which is described below, yielded information that permits an approximation of the curve. This curve is shown in Fig. 10. The results of the work were briefly described in an article by Buchholtz and Köster,[257] and Dr. Köster was kind enough to supply additional information in a private communication.

According to Köster, the solubility of copper in iron at temperatures below 600°C. is approximately 0.4 per cent, since alloys

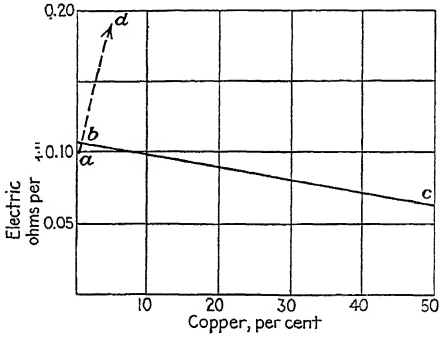


FIG. 11.—Electric resistivity of iron-copper alloys. (*Köster.*)

containing more than this amount of copper respond to a precipitation-hardening treatment, and those containing less copper do not. As Köster pointed out, this is probably an effective limit of solubility and not the real limit, which might be found to be nearer 0.1 per cent copper, if exceedingly long times were allowed for the precipitation to proceed. For estimating the line in question Köster used an alloy containing 5 per cent copper. Samples of this alloy were quenched from different temperatures between 600 and 900°C. and their electric resistivity was determined. As copper is added to iron in amounts that form a solid solution in alpha iron, the resistivity should change as shown by curve *ad* in Fig. 11. Point *b*, at 0.4 per cent copper, on this curve represents the limit of solubility of copper in iron at low temperatures. For alloys in equilibrium the resistivity should change along lines *ab* and *bc*. When alpha iron at room temperature is supersaturated with copper and all of the copper is in solid

solution, the resistivity should fall on line *bd*. If alloys containing 5 per cent or more copper are quenched from a temperature above 600°C., their resistivity should fall on a line approximately parallel to line *bc*, and the intersection of this line with line *bd* should give the approximate composition of the iron-rich phase at the quenching temperature. It should be pointed out that *bc* probably is not a straight line and that the method used in estimating the solubility line is open to question, even though it probably gives a fair estimate of the line.

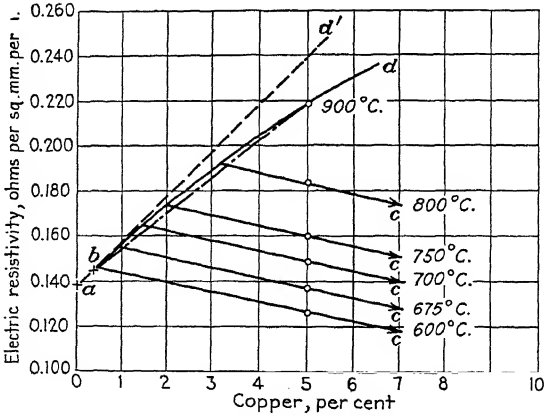


FIG. 12.—Electric resistivity of low-copper iron-copper alloys. (*Köster.*)

The specific resistivities of the 5 per cent copper alloy quenched from different temperatures are shown by the circles in Fig. 12. In the figure the resistance of iron is shown as 0.138 instead of 0.10 in order to account for the impurities in the alloy. A series of observations at Vereinigte Stahlwerke has shown that for small amounts of copper the resistance of iron is increased at the rate of 0.02 ohm per sq. mm. per m. for each per cent of copper. If this rate is constant up to 5 per cent copper, the resistance of iron-copper alloys should fall along line *ad'* in Fig. 12. The alloy containing 5 per cent copper, however, had a lower resistance than indicated by this line. A better line is, therefore, *ad*, drawn with some curvature. The resistivity of alloys quenched from 600°C. should be given by line *ab* and a straight line passing through the point giving the resistivity of the 5 per cent alloy quenched from 600°C. Point *b* is on curve *ad* and at 0.4 per cent copper. Lines parallel to the one just mentioned and passing

through resistivity values obtained by quenching from other temperatures intersect *ad* at compositions giving the concentration of copper in the iron-rich phase. The solubility curve thus located is shown in Fig. 10.

The solubility curve determined by Köster and associates indicates that 3.5 per cent copper is soluble in alpha iron at the eutectoid temperature. Ruer and associates placed the eutectoid concentration at only 2.3 per cent. Obviously the eutectoid must contain more copper than is soluble in alpha iron at the eutectoid temperature. Köster estimated that the eutectoid is between 4 and 5 per cent copper. In reference to the eutectoid temperature, Köster found that a 5 per cent copper alloy showed a transformation interval between 810 and 845°C. and was not able to determine the true equilibrium temperature. Although he has given an illustration showing the temperature as 810°C., he believes that the temperature of 833°C., given by Ruer, should be considered as the more probable until other data are available.

As a result of some work on the solubility of copper in iron, Smith* concluded that the values obtained by Buchholtz and Köster need some modification. He found the solubility at 800°C. to be somewhat over 1 per cent, and probably a little less than 2 per cent at the eutectoid temperature, which he placed at 843°C. These values ensued from the following considerations. A series of electric-conductivity determinations on an alloy containing 0.91 per cent copper showed that copper commenced to precipitate at about 760°C., whereas Buchholtz and Köster indicated the alpha boundary to be at about 680°C. for an alloy of this composition. The alloys used by Smith were prepared from ingot iron; melting was under highly oxidizing conditions in a small high-frequency furnace, and although about 0.1 per cent manganese and 0.4 per cent silicon were added the final alloys contained only about 0.04 per cent manganese and 0.1 per cent silicon. Cooling curves, taken at a rate of about 4°C. per min. on an alloy containing 4.01 per cent copper, 0.011 per cent carbon, 0.068 per cent manganese, and 0.026 per cent silicon, annealed for prolonged periods at high temperatures, showed an arrest at 824°C. only when the maximum annealing temperature had been above 844°C., and the arrest was found to disappear when a specimen annealed at 900°C. was held at 839°C. for 1 hr. before cooling further. This and other thermal data indicated

* Unpublished report by C. S. Smith of the American Brass Company.

the eutectic temperature to be at about 843°C. Heating curves showed an arrest at 856°C., indicating a lag of about 32°C. between heating and cooling.

The hardness of quenched specimens obtained by Smith indicated a rather low eutectoid temperature, since on quenching from 830°C. some gamma iron was apparently formed. The effect of quenching from various temperatures on the Rockwell hardness of samples containing 2.49 and 4.01 per cent copper is shown in Fig. 13. The break in the curves between 800 and 850°C. was

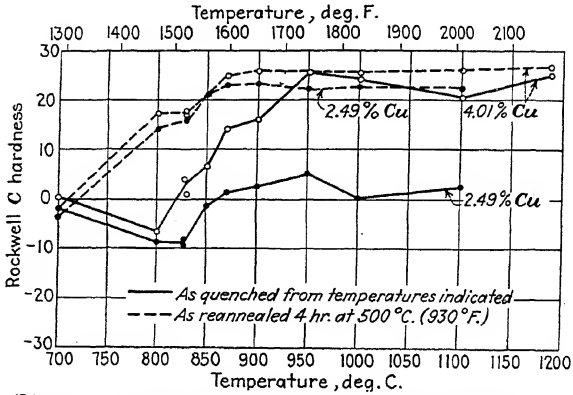


FIG. 13.—Effect of quenching and tempering on Rockwell hardness of iron-copper alloys. (*Smith.*)

attributed to the formation of some gamma iron (which on quenching breaks down to alpha iron supersaturated with copper). The hardness after the precipitation treatment (heating 4 hr. at 500°C.), shown by the dotted curves in Fig. 13, is about the same for the 2.5 and 4 per cent alloys, although there is a great difference in the quenched state.

The solid solubility of iron in copper was determined independently by Hanson and Ford[143] and by Tammann and Oelsen.[272] By microscopic examination of carefully prepared samples quenched from different temperatures, Hanson and Ford obtained the results shown diagrammatically in Fig. 14. It may be seen from the curve that the solubility of iron in copper falls rapidly from about 4 per cent at 1100°C. to less than 0.2 per cent at 750°C. Below 750°C. the change in solubility is very slight. Hanson and Ford attributed the abrupt change at 800°C. to the gamma-alpha transformation taking place in

the precipitated iron-rich phase. From this they concluded that copper is in equilibrium with gamma iron above the trans-

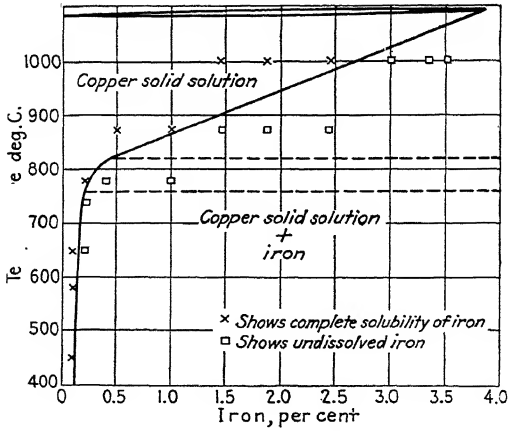


FIG. 14.—Solubility of iron in copper. (*Hanson and Ford.*[143])

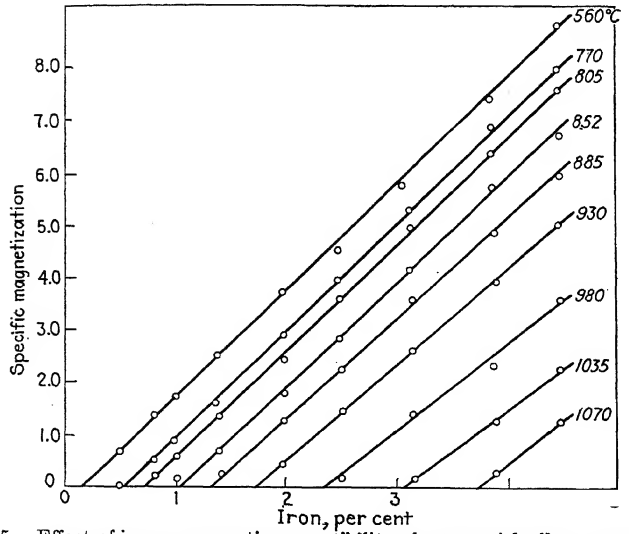


FIG. 15.—Effect of iron on magnetic susceptibility of copper-rich alloys quenched from temperatures shown. (*Tammann and Oelsen.*[272])

formation point and with alpha iron below this temperature. This explanation of the abrupt increase in solubility above 800°C. is supported by the fact that above 800°C. both con-

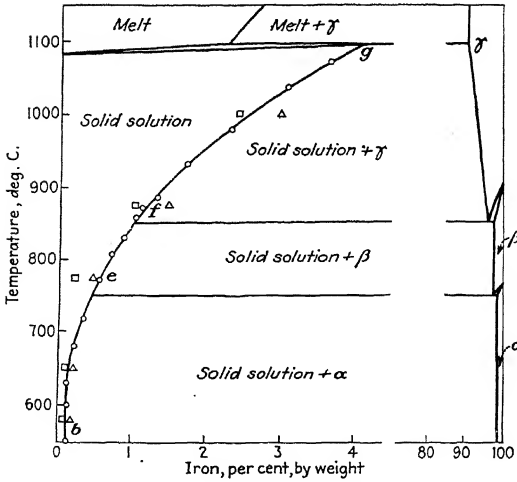


FIG. 16.—Solubility of iron in copper. (*Tammann and Oelsen.*[272])

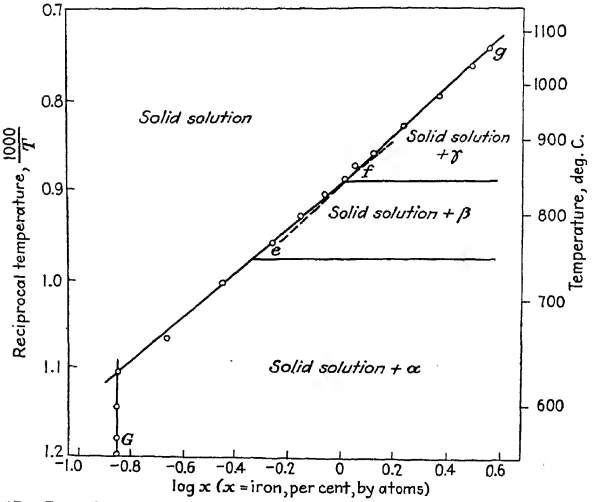


FIG. 17.—Logarithmic curve of solubility of iron in copper. (*Tammann and Oelsen.*[272])

stituents, gamma iron and copper, crystallize in the face-centered cubic lattice.

Tammann and Oelsen sought the solubility curve of iron in copper by measurements of intensity of magnetization on a series of quenched alloys. Values plotted against the concentration of iron gave straight lines for every temperature (Fig. 15). The iron concentration of the saturated solid solution at respective temperatures was taken as the concentration indicated by the intersection of these straight lines with the concentration axis. These values plotted on the temperature-concentration diagram gave the solubility line shown in Fig. 16. Although the results are numerically not very different from those obtained by Hanson and Ford (Fig. 14), Tammann and Oelsen's curve appears much smoother, although it has two breaks, one at 850°C. and the other at 755°C. These are hardly noticeable in Fig. 16; however, the break at 850°C. is shown more clearly in their logarithmic curve (point *f*, Fig. 17). An inflection in hardness-versus-quenching-temperature curves of iron-rich alloys was also observed at about 850°C. by Kussmann and Scharnow[238] and Isihara.[131] The supposed break at 755°C. was attributed by Tammann and Oelsen to loss of magnetism in the saturated iron-rich solution. The heat effect of this transformation and correspondingly the discontinuity in the solubility line is, however, very slight. This is also in agreement with the results of Kussmann and Scharnow.

As may be seen from the curve in Fig. 16, Tammann and Oelsen gave the solubility of iron in copper as 4.0 per cent at 1094°C. and falling gradually to 0.14 per cent at 600°C. Below the latter temperature the solubility line is vertical owing to the fact that equilibrium is never reached, because the precipitation is so slow that the solubility appears to be independent of the temperature. The solubility at room temperature was, therefore, taken as 0.14 per cent, although extrapolation indicates a solubility of 5.9×10^{-11} per cent at 20°C.

In a recent study Kussmann and Seemann[293,324] found that the change of copper from the diamagnetic to the paramagnetic state upon cold working "pure" copper is due to the precipitation of iron. They found the susceptibility after cold working to be dependent on the iron content (at least up to 2.3×10^{-4} per cent iron) and also to vary with the field strength, whereas the susceptibility of the annealed material is independent of iron

content and does not change with field strength. The susceptibility of brass changed on cold working, but no change was observed for aluminum, gold, zinc, tungsten, molybdenum, or nickel brass, in all of which iron is soluble even at room temperatures.

The change in susceptibility of copper on cold working was apparently discovered by Bitter[256] and later confirmed by Honda and Shimizu,[262] Lowance and Constant,[296] and Shimizu,[377] while Banta[277] could not find the effect. Shimizu showed that, when correction is made for ferromagnetic impurity by extrapolating to infinite field strength, copper actually becomes more strongly diamagnetic on cold working ($\chi = -0.163 \times 10^{-6}$ for fully cold-worked copper as compared with -0.085×10^{-6} for annealed copper). Although Shimizu, and Heaps and Banta,[290] accepted the precipitation theory of Kussmann and Seemann, Lowance and Constant rejected it on account of the supposed purity of their copper.

Results of an investigation of the effect of iron on the electric conductivity of copper by Heuer[184] seem to indicate that copper dissolves about 0.3 to 0.4 per cent of iron in the solid state at room temperature.

C. THE PROBABLE EQUILIBRIUM DIAGRAM

What is believed to be the most probable equilibrium diagram of the iron-copper system is shown in Fig. 18. Uncertain lines are dashed, but the fact that a line is solid does not mean that it has been satisfactorily located. The diagram is essentially the one drawn by Ruer and associates modified to show the miscibility gap closed above the liquidus.

16. Liquid Immiscibility.—There is sufficient experimental evidence to prove that a miscibility gap exists in the iron-copper system but that the two-liquid region does not intersect the liquidus. The two-liquid region expands with increasing temperature. It is probably closed at about 20°C. above the liquidus. All iron-copper alloys, therefore, melt to form a single liquid, but for alloys containing from 15 to 90 per cent copper two liquid layers are formed as the temperature of the melt is increased.

17. Equilibria Involving Delta Iron.—The field of homogeneous delta is *AHG* in Fig. 18. The addition of copper to iron lowers the melting point along line *AB*, where melt is in equilibrium

with delta along line AH. Melt at B is in equilibrium with delta at H (6.5 per cent copper) and gamma at I. The peritectic reaction at the horizontal HIB, 1477°C., is analogous to the reaction in the iron-carbon system involving delta and gamma iron. Field AHB contains melt and delta. The field HIG contains delta plus gamma. The lines AB, HIB, and GH have

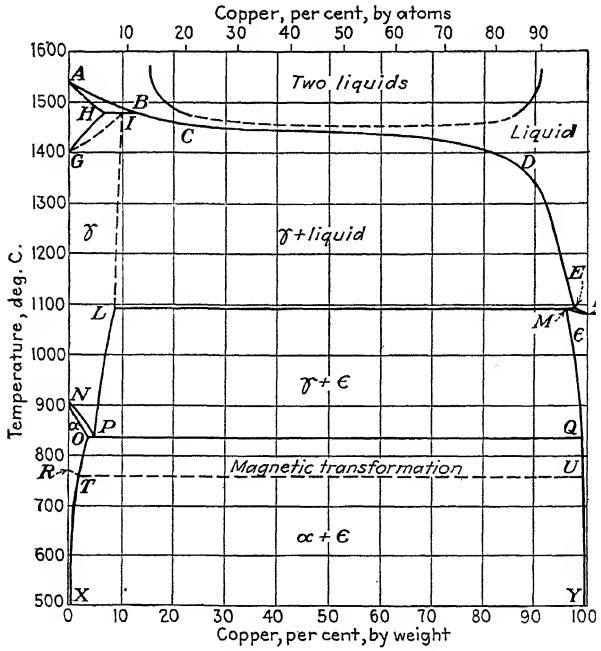


FIG. 18.—Proposed equilibrium diagram of the iron-copper system.

been accurately located. Point I has not been experimentally located, and the lines AH and GI are drawn where they would be expected to be found and not through experimentally determined points.

18. Other Equilibria Involving a Liquid.—The branch of the liquidus AB was mentioned above. The second branch of the liquidus is shown as $BCDE$. Along this branch melt is in equilibrium with gamma along line IL. A portion of the liquidus is almost horizontal, which is reasonable in view of the miscibility gap shown. The portion of the liquidus under discussion has been rather accurately located. Line IL, however, is unsatis-

factory. Point *L* is near 9 per cent copper, but the position of point *I* is uncertain. If the line slopes in the direction as drawn, which seems probable but not certain, some liquid is formed from a solid on cooling.

The third branch of the liquidus is *EF*, along which melt is in equilibrium with epsilon (copper dissolving iron) along line *MF*. Point *E* is at 2.5 per cent iron and 1094°C. Point *M* is at 4 per cent iron and necessarily at 1094°C. The temperature of 1094°C. seems to be well established, and the compositions at points *M* and *E* are known with some certainty.

At the peritectic temperature of 1094°C. melt at *E* is in equilibrium with gamma at *L* and epsilon at *M*. Alloys in the field below *LMF* are completely solid.

19. Equilibria in the Solid.—The field of homogeneous gamma is outlined on the low-temperature side by lines *NP* and *LP*. Along *NP* gamma is saturated with alpha along *NO*. Along *LP* gamma is saturated with epsilon along *MQ*. The concentration of the eutectoid *P* is 2.3 per cent according to Ruer and coworkers, and the eutectoid temperature is 833°C. Other work, however, indicates that point *O* is at 3.5 per cent copper. This point must be to the left of *P*, unless the reaction is a peritectoid instead of a eutectoid as shown, which seems improbable. It seems reasonable to accept Köster's guess that *P* is between 4 and 5 per cent copper; it was drawn at 4.5 per cent copper and *O* at 3.5 per cent copper. Line *OX* represents the limit of solubility of copper in iron. At temperatures below 600°C., *OX* is to the left of 0.4 per cent copper (Fig. 10).

Line *MQUY*, representing the solubility of iron in copper, has been rather accurately determined, and reference should be made to Figs. 14 and 16 to determine its exact location.

The addition of copper to iron decreases the temperature of the magnetic transformation 10°C., as shown by line *RT*. The temperature of the magnetic transformation for alloys containing more than enough copper to saturate the iron at 758°C. naturally does not vary with composition (line *TU*).

D. AUTHORS' SUMMARY

The equilibrium diagram for the system iron-copper has been worked out, although several points still remain to be ascertained. Figure 18 represents a composite diagram based on the best information available in the literature.

1. It may be seen from the diagram that iron and copper are only partially soluble both in the liquid and in the solid state. The liquid miscibility gap closes at about 20°C. above the liquidus, the solubility decreasing with rising temperature, at least up to 1575°C.

2. In the solid state the alloys may consist either of homogeneous solid solutions of the one metal in the other or of heterogeneous mixtures of these solid solutions.

3. At 400°C. alpha iron dissolves 0.4 per cent copper, and at 833°C. about 3.5 per cent. Gamma iron dissolves 4.5 per cent copper at 833°C., 8.5 per cent at 1094°C., and possibly about 10 per cent at 1477°C. Copper dissolves 4 per cent iron at 1094°C. and 0.14 per cent or less at room temperature.

4. The solubility of liquid copper in gamma iron presumably increases with rising temperature, and, therefore, the alloys containing from 8.5 to about 10 per cent copper are subject to liquation on cooling.

5. There has been a disagreement between Ruer and his coworkers on one side, and Müller, Ostermann, and others on the other side, regarding the mutual solubility of iron and copper in the liquid state. The former advocate the existence of the liquid miscibility gap intersecting the liquidus, and the latter maintain that the metals are soluble in all proportions just above the liquidus. The suggestion of Benedicks regarding the influence of carbon and other impurities on the position of the lower critical point of the liquid-solubility curve has tended to settle the controversy. However, it appears that a further study of this question is needed wherein particular attention should be given to obtaining equilibrium conditions of the alloys under investigation. From early work and from recent unpublished work there is some evidence that two liquids are not formed at any temperature or concentration, and further study of liquid alloys of high purity is needed.

6. Other parts of the diagram that have not been definitely established and need experimental study are:

a. The position of point *I* and line *GI* (Figs. 18, 2), representing the end of the delta-gamma transformation.

b. The position of point *K* and line *IK* (Fig. 2), representing the freezing temperatures of the alloys solidifying along portion *BC* of the liquidus.

c. The exact location of line *LI* (Fig. 18), indicating the extent of the gamma solid solutions at high temperatures. This line is of particular interest in connection with the liquation of high-copper steels.

d. The eutectoid and the limit of solubility of copper in alpha iron for the low-temperature, iron-rich portion of the diagram have not been adequately investigated, and this is probably the most important part of the diagram.

CHAPTER III

CONSTITUTION OF IRON-COPPER-CARBON ALLOYS

The Systems Iron-cementite and Cementite-copper—Iron-copper-cementite Diagram Suggested by Ishiwara and Coworkers—Results of Experimental Study—Authors' Summary

With the exception of a few scattered observations, the only available information on the iron-copper-carbon system is that in an article by Ishiwara, Yonekura, and Ishigaki[166] published in 1926. These Japanese investigators constructed a diagram that meets the requirements of the phase rule and attempted to locate certain regions in the diagram by an experimental study of iron-rich alloys containing as much as 30 per cent copper; but their experimental data are not adequate for the definite location of the important regions in even the iron-rich corner. The ternary diagram suggested by Ishiwara and coworkers will be outlined below, and the experimental observations will then be discussed.

A. THE SYSTEMS IRON-CEMENTITE AND CEMENTITE-COPPER

The binary system iron-copper has been discussed in detail in the preceding chapter. The iron-cementite diagram and a postulated copper-cementite diagram are discussed below.

20. The Fe-Fe_3C Diagram.—Two diagrams for iron-carbon alloys have been proposed—one, a so-called metastable diagram, in which the components are iron and iron carbide (cementite), the other, a stable diagram, in which the components are iron and graphite. The former diagram will be used in outlining the possible ternary diagram, for no cognizance will be taken of the existence of graphite in iron-copper-carbon alloys.

As previously mentioned, the iron-rich portion of the iron-cementite diagram is strikingly similar to that of the iron-copper diagram. In both diagrams the field of gamma iron is widened; there is a peritectic reaction between the phases delta, gamma, and melt, and the existence of the gamma phase is limited below by a eutectoid horizontal.

21. The Possible Cu-Fe_3C Diagram.—Owing to the instability of iron carbide (cementite), it has not been possible to determine the phase diagram copper-cementite. As almost nothing is known in regard to the behavior of alloys formed between cementite and copper, it may be instructive to consider the ability of copper to absorb carbon. The solubility of carbon in molten copper was alleged by Matthiessen (according to Guertler[46]) to be 0.05 per cent. Hempel[43] thought that the solubility of carbon in molten copper was between 0.02 and

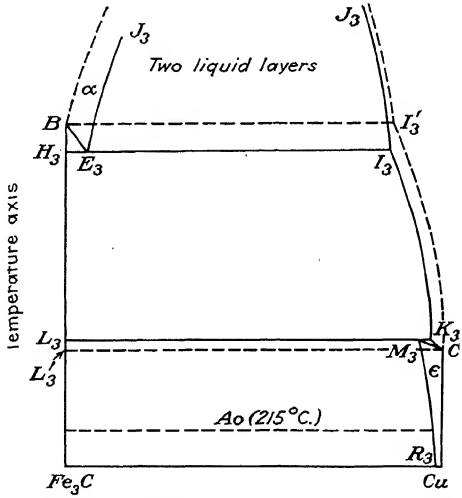


FIG. 19.—Copper-cementite diagrams. (*Ishiwara, Yonekura, and Ishigaki.*[166])

0.03 per cent. As reported by Guertler,[71] Kurnakow and Zhemchuzhny observed graphite between grains of copper that had been melted with charcoal. But in many instances copper or copper-rich alloys are melted in contact with carbon, and no evidence has been brought forth to show that these materials absorb carbon unless a third element is present which does absorb carbon. When copper free from oxygen is produced by melting in contact with carbon, the copper does not retain enough carbon to protect it against the small amount of oxygen absorbed on pouring in the air. While no exact data on the solubility of carbon in molten copper are available, it may be safe to estimate that the solubility is less than 0.005 per cent.

By analogy one might assume that cementite and copper do not readily alloy.

Possible copper-cementite diagrams suggested by Ishiwara and coworkers are shown in Fig. 19. The solid lines represent the diagram that they used in working out a possible ternary diagram. It was assumed that there is an extended range of liquid immiscibility in the system. According to the diagram shown by the solid lines, copper lowers the melting point of cementite, and the copper-rich portion of the diagram is similar to that of the iron-copper diagram. The dotted lines are for a system in which copper does not lower the melting point of cementite and in which a eutectic is formed between copper and cementite, the eutectic containing a negligible amount of copper and melting at approximately the same temperature as copper.

For dealing with alloys near the iron corner of the ternary diagram, an exact knowledge of the copper-cementite diagram is unimportant. The really important part of the diagram is the region of liquid immiscibility, and it is safe to assume that it is extensive.

B. IRON-COPPER-CEMENTITE DIAGRAM SUGGESTED BY ISHIWARA AND COWORKERS

An outline of the iron-copper-cementite diagram can be prepared from a consideration of the pertinent binary diagrams and a knowledge of the behavior of a few ternary alloys. The general features of the ternary diagram will be outlined below, and the experimental data having to do with the diagram will be discussed later.

22. General Features of Diagram.—Study of the related binary systems indicates that seven phases must be accounted for in the ternary system Fe-Cu-Fe_3C. These phases are: (1) liquid *A*, the iron-rich liquid, (2) liquid *B*, the copper-rich liquid, (3) delta phase, the high-temperature modification of iron, (4) gamma phase, austenite, (5) alpha phase, ferrite, (6) epsilon phase, the copper-rich solid solution, and (7) iron carbide (Fe_3C), cementite. In the system under discussion it is desirable to consider alpha and delta iron as distinct phases, because they never merge as they do in binary systems having a closed gamma loop or in ternary systems in which at least one of the binary systems has a closed gamma loop.

The extended regions of liquid immiscibility in the iron-copper and copper-cementite systems make it apparent that the region of liquid immiscibility in the ternary system covers most of the field. The Japanese workers assumed that in the iron-copper system the field of liquid immiscibility intersects the liquidus and drew their ternary diagram accordingly. This assumption,

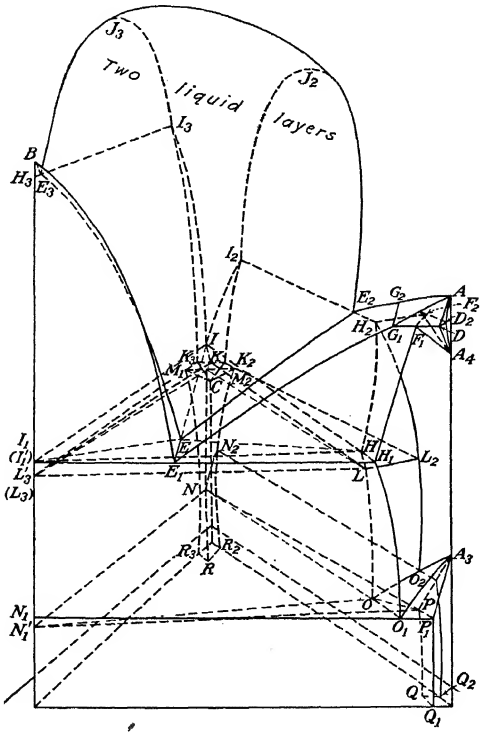


FIG. 20.—The iron-copper-carbon diagram according to *Ishiwara, Yonekura, and h*

as pointed out in the preceding chapter, is very probably incorrect. If the field of immiscibility lies above the liquidus in the iron-copper system and is widened with increasing temperature, the ternary diagram suggested by the Japanese investigators must be modified to show a two-liquid region similar to that shown by Tammann[151] for the system water-phenol-triethylamine.

The space model of the diagram drawn by the Japanese workers is shown in Fig. 20, and the projections of intersections of reaction surfaces on the concentration plane are shown in Fig. 21. This diagram should be modified to show the two-liquid region just failing to touch the iron-copper liquidus, and such a modification necessitates changes in portions adjacent to the iron-copper edge. The diagram shown in Figs. 20 and 21 may be considered as a

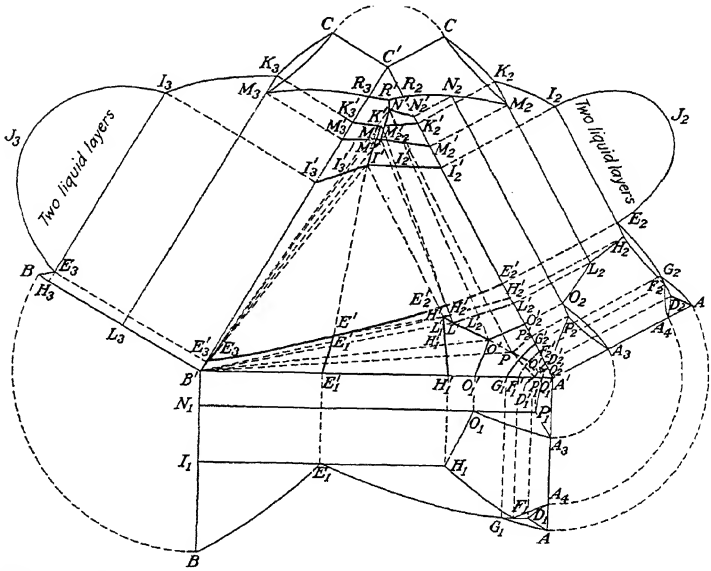


FIG. 21.—Projections of intersections of reaction surfaces of the iron-copper-carbon diagram. (*Ishiwara, Yonekura, and* .

simplification of the real diagram, and no attempt will be made to show the more complicated diagram in which the immiscibility region does not intersect the iron-copper liquidus.

23. Reactions Involving Delta Iron.—In both the iron-carbon and iron-copper systems the following invariant reaction occurs:

$$\text{Delta} + \text{liquid} = \text{gamma}$$

This reaction also occurs in the ternary system but differs in that it is univariant; it is not consummated at a constant temperature. During the reaction the composition of the melt lies along line G_1G_2, that of the delta phase along line D_1D_2, and that of the resultant gamma phase along line F_1F_2 (Fig. 21).

The univariant reaction just mentioned indicates that the delta phase cannot exist in equilibrium with liquid at a temperature just below the minimum temperature along line G_1G_2. The region of homogeneous gamma is limited at the high-temperature side by the line F_1F_2.

24. Other Reactions Involving Liquid Phases.—As previously mentioned, the two-liquid region in the ternary system does not intersect the iron-copper liquidus. The observations of a number of the earlier workers, however, indicate that it is not far removed from the iron-copper liquidus. In considering alloys containing even small quantities of carbon, no real discrepancy will result from considering the two-liquid region to be as shown by the diagram of Ishiwara and associates.

Line E_1E, along which liquid, cementite, and gamma phase are in equilibrium, intersects what will be called a "monotectic line" (E_3EE_2). A monotectic line is a line along which two liquid phases are in equilibrium with a solid phase. Melt of a composition along E_1E is in equilibrium with cementite of an assumed constant composition and gamma phase whose composition is represented by line H_1H. Line E_3E is a monotectic line representing the composition of the iron-rich melt in equilibrium with cementite of a constant composition and the copper-rich melt along line I_3I. Line E_2E is a monotectic line representing the composition of the iron-rich melt in equilibrium with gamma phase of a composition along line H_2H and copper-rich melt of a composition along line I_2I.

Melt of composition E is in equilibrium with cementite, gamma phase represented by point H, and the copper-rich melt represented by point I. As four phases are present, an invariant reaction must occur and must proceed at a constant temperature until one phase disappears. The reaction is:

$$\text{Melt } (E) = \text{gamma } (H) + \text{cementite} + \text{melt } (D)$$

The reaction thus differs from a ternary eutectic reaction in that one liquid phase and two solids, instead of three solid phases, are formed from a liquid phase on cooling.

Alloys near the iron corner will solidify without the formation of a copper-rich liquid, but in others lying within the field ABE_3E_2 either iron or cementite will separate primarily, and a copper-rich melt will form when the remaining liquid has reached a composition along line E_3EE_2. Alloys of certain composition,

therefore, can contain two liquid phases at some temperatures, even though they lie outside the liquid immiscibility region. The line dividing the region in which a second melt is formed on cooling from that in which only an iron-rich phase and cementite separate on cooling depends on the extent of the gamma region at high temperatures. There is so much uncertainty regarding the extent of the gamma region that the location of the line just mentioned is not known.

Ishiwara and coworkers completely outlined the probable behavior in the copper-rich regions during solidification, but there is little to be gained by a detailed discussion of this part of the diagram. The reactions postulated can be determined from the diagram shown in Figs. 20 and 21. According to the diagram, only two copper-rich phases are possible; they are a liquid and solid copper containing small amounts of iron and carbon. The copper-rich melt of a composition *K* disappears in the reaction:

$$\text{Melt} + \text{gamma} + \text{cementite} = \text{epsilon}$$

During this reaction melt of composition *K* is in equilibrium with the gamma phase of composition *L*, cementite, and the epsilon phase (copper) of composition *M*.

25. Reactions in the Solid State.—At temperatures above the alpha-gamma transformation temperature of iron and below the temperature of the invariant reaction just mentioned, only three phases exist. These are cementite, gamma, and epsilon. The epsilon phase contains a small amount of iron and possibly a small amount of carbon at elevated temperatures. Under equilibrium conditions at ordinary temperatures it contains practically no carbon and very little iron. When dealing with equilibria in solid iron-rich alloys it is justifiable to consider the epsilon phase as consisting of pure copper at all temperatures.

Because the gamma phase in the binary systems iron-carbon and iron-copper disappears at eutectoid transformations on cooling, it must disappear at an invariant reaction in the iron-copper-carbon system, unless cementite and copper form a continuous series of solid solutions. Copper and cementite certainly are not mutually soluble in all proportions in the solid state, and an invariant reaction must occur. This reaction is eutectoid, as was shown by Ishiwara and coworkers.

According to Fig. 20, alpha iron separates from gamma iron on surface $A_3O_1OO_2$, cementite separates on surface H_1O_1OLH, and copper on surface L_2LOO_2. The lines of double saturation of the gamma phase are O_1O, LO, and O_2O. Point O is the point of triple saturation at which gamma iron of composition O is in equilibrium with alpha iron of composition P, cementite, and copper. The reaction is:

$$\text{Gamma} = \text{alpha} + \text{cementite} + \text{copper}$$

The reaction proceeds at a constant temperature until the gamma iron disappears.

The shape of the alpha region is readily seen from Fig. 20. The extent of this region is of importance in reference to precipitation-hardening phenomena, but its limits have not been satisfactorily determined.

C. RESULTS OF EXPERIMENTAL STUDY

It now remains to locate the surfaces on the ternary diagram outlined. Unfortunately, so few experimental results are available that it is impossible to locate many of the surfaces even approximately. With the exception of those obtained by Ishiwara and coworkers, there are almost no data that are helpful in constructing the actual diagram, and even these are not at all adequate for constructing even the iron-rich portion of the diagram.

26. The Immiscibility Region.—The Japanese investigators attempted to locate the portion of the monotectic line near the iron-rich corner by microscopic examination of cast specimens to determine whether or not the specimens had consisted of two liquid layers. Figure 22 shows the line which they constructed from these observations. The composition of the alloys examined and the results of the examinations may be determined from the figure. Points a and b represent analyses of the iron-rich layer of alloys prepared by melting pig iron with sufficient copper to form two liquid layers and cooling rapidly. Point c was obtained by plotting the arrest temperatures observed on cooling alloys containing 3.5 per cent carbon and drawing smooth curves through the points. The curves used in locating point c were not at all well defined by the experimental points and are of questionable value for locating a point on the monotectic line. Figure 23 shows the curves as plotted; point c should lie on the monotectic line.

The points shown as crosses in Fig. 22 represent the composition of the iron-rich layers of melts containing excess copper

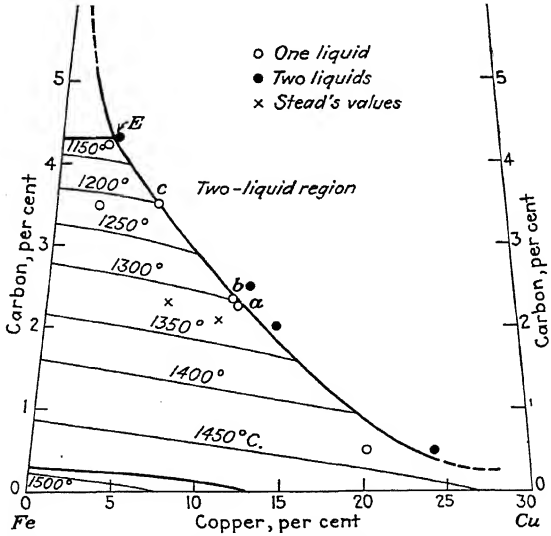


FIG. 22.—The liquid immiscibility region of iron-rich alloys of iron, copper, and carbon. (*Ishiwara, Yonekura, and*.

as reported by Stead.[39] Stead's values are possibly too far removed from the copper corner, since some of the copper-rich

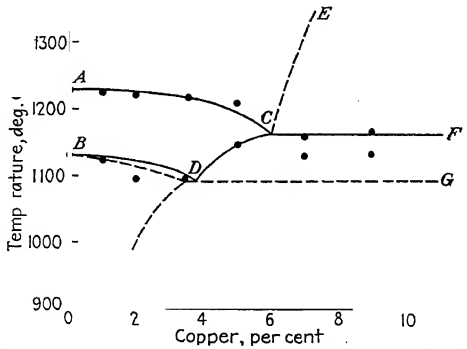


FIG. 23.—Thermal-analysis data on a section of the ternary diagram through 3.5 per cent carbon. (*Ishiwara, Yonekura, and*.

liquid formed during solidification probably settled into the copper-rich layer.

Point *E* (Fig. 22) is the intersection of the line along which the binary eutectic iron-cementite is formed and the monotectic line. Microscopic examination of several specimens indicated that the addition of a few per cent copper to iron-carbon alloys of a eutectic composition did not result in the appearance of either excess carbide or excess iron. It was, therefore, assumed that the line along which the melt is saturated with both cementite and gamma phase is parallel to the iron-copper side. If that is the case, point *E* is at 4.3 per cent carbon and between 3.0 and 3.5 per cent copper.

27. Arrest Points on Cooling from the Liquid.—The Japanese workers prepared alloys containing as much as 3.5 per cent carbon and 30 per cent copper from pig iron, wrought iron, and electrolytic copper. Alloys of higher copper content were not used, because the melt separated into two liquid layers. Cooling curves were made with specimens weighing 30 g., and the arrest points are shown in Table 5. The calculated compositions shown in this table may be nearer the actual composition of the melt than those obtained by analysis, on account of the difficulty in obtaining a representative sample from a heterogeneous specimen.

The isothermals shown in Fig. 22 were derived from the arrest points given in Table 5. The second arrest, at approximately 1100°C., shown in alloys containing 12 per cent or more copper and not over 1.5 per cent carbon, was attributed to the reaction:

$$\text{Copper-rich melt} + \text{gamma} = \text{epsilon}$$

This reaction is similar to the peritectic reaction near 1100°C. in the system iron-copper. The second arrest in alloys containing over 1.5 per cent carbon, which also occurs at approximately 1100°C., was attributed to the invariant reaction involving melt at *E*. This indicates that the iron-cementite eutectic falls from 1130 to 1100°C. on the addition of approximately 3 per cent copper.

The third arrest observed on cooling from the liquid results from the gamma to alpha transformations, but the temperatures given are of little use in establishing the lower limits of the gamma phase.

28. Reactions in Solid Alloys.—From microscopic examination it was concluded that the addition of small amounts of copper to iron-carbon alloys did not change the maximum solubility of

TABLE 5.—ARREST POINTS OBSERVED ON COOLING IRON-COPPER-CARBON ALLOYS*

Specimen number	Composition, per cent				Arrests, °C.		
	C calculated	Cu calculated	C by analysis	Cu by analysis	First arrest	Second arrest	Third arrest
1	0.05	0.0	....	0.0	1522		
2	0.05	1.0	....	0.9	1526	....	830
3	0.05	2.5	....	2.8	1511	....	764
4	0.05	3.5	....	3.2	1505	....	753
5	0.05	5.0	....	4.5	1490	....	740
6	0.05	7.0	....	6.2	1488	....	736
7	0.05	9.0	....	....	1473	....	731
8	0.05	12.0	....	....	1477	....	750
9	0.05	15.0	....	14.7	1466	....	720
10a	0.05	20.0	....	20.5	1443	....	725
10b	0.05	25.0	....	....	1449	1098	730
10c	0.05	30.0	....	....	1446	1099	725
11	0.5	0.0	....	....	1490	....	708
12	0.5	1.0	....	....	1472	....	679
13	0.5	2.5	0.48	2.4	1475	....	677
14	0.5	3.5	0.42	3.1	1466	....	675
15	0.5	5.0	....	5.0	1423?	....	675
16	0.5	7.0	0.38	6.7	1455	....	675
17	0.5	9.0	0.37	8.2	1460	....	676
18	0.5	12.0	0.42	11.2	1436	....	676
19	0.5	15.0	0.41	14.0	1435	1073	674
20a	0.5	20.0	0.46	17.7	1418?	1055?	676
20b	0.5	25.0	....	....	1435	1096	650
20c	0.5	30.0	....	....	1425	1091	645
21	1.0	0.0	....	....	1450	....	715
22	1.0	1.0	1.10	....	1429	....	710
23	1.0	2.5	0.83	2.2	1450	....	685
24	1.0	3.5	0.89	3.1	1452	....	685
25	1.0	5.0	1.09	4.7	1449	....	670
26	1.0	7.0	1.00	6.6	1419	....	685
27	1.0	9.0	0.95	8.1	1432	....	685
28	1.0	12.0	1.10	11.6	1412	1095	687
29	1.0	15.0	1.10	11.5	1421	1087	685
30	1.0	20.0	1.09	....	1390	....	667
31	1.5	0.0	1.47	0.0	1417	....	715
32	1.5	1.0	1.32	0.7	1415	....	694
33	1.5	2.0	1.35	1.5	1412	....	685
34	1.5	3.5	1.50	2.9	1411	....	680
35	1.5	5.0	1.43	4.0	1411	....	678
36	1.5	7.0	....	....	1365	....	676
37	1.5	9.0	1.28	8.3	1355	....	665
38	1.5	12.0	....	....	1365	....	670
39	1.5	15.0	....	....	1365	1068	675
40	1.5	20.0	1.56	15.5	1363	1078	680

TABLE 5.—ARREST POINTS OBSERVED ON COOLING IRON-COPPER-CARBON ALLOYS.*—(*Continued*)

Specimen number	Composition, per cent				Arrests, °C.		
	C calculated	Cu calculated	C by analysis	Cu by analysis	First arrest	Second arrest	Third arrest
41	2.0	0.0	1.97	0.0	1369	....	697
42	2.0	1.0	2.01	0.7	1367	1065	693
43	2.0	2.0	....	2.6	1364	1055	683
44	2.0	3.5	1.89	3.0	1362	1074	678
45	2.0	5.0	2.37	5.3	1347	1080	676
46	2.0	7.0	1.90	6.3	1349	1078	676
47	2.0	9.0	2.27	9.0	1348	1079	673
48	2.0	12.0	2.04	13.3	1338	1077	674
49	2.0	15.0	2.13	15.4	1326	1079	672
50	2.0	20.0	2.12	9.9	1325	1080	673
51	2.5	0.0	....	....	1331	1129	724
52	2.5	1.0	2.25	0.9	1326	1096	703
53	2.5	2.0	....	....	1320	1118	695
54	2.5	3.5	2.45	3.1	1311	1091	679
55	2.5	5.0	....	....	1311	1089	681
56	2.5	7.0	2.51	6.6	1277?	1080?	671
57	2.5	9.0	2.39	8.0	1291	1092	682
58	2.5	12.0	....	12.5	1283	1110	678
59	2.5	15.0	2.51	8.7	1275	1108	680
60	2.5	20.0	....	....	1255	1104	679
61	3.5	0.1	3.62	....	1228	1132	725
62	3.5	1.0	3.37	0.9	1224	1122	720
63	3.5	2.0	3.50	2.0	1220	1093	715
64	3.5	3.5	3.42	3.8	1217	1093	710
65	3.5	5.0	3.68	4.6	1207	1143?	690
66	3.5	7.0	3.69	5.1	1156	1128	682
67	3.5	9.0	3.95	8.5	1162	1130	680
68	3.5	12.0	3.53	....	1168	....	678
69	3.5	15.0	3.57	10.4	1163	....	678

* Ishiwara, Yonekura, and Isnig

carbon in gamma iron. If this is true, point *H*, shown in Figs. 20 and 21, lies on a line parallel to the iron-copper side and passing through the point 1.7 per cent carbon on the iron-cementite side. A line through point *D*, obtained from Fig. 23 and passing through point *E*, should also pass through point *H*. Determined by such a method, *H* is at 1.7 per cent carbon and 6 per cent copper. It appears to the authors that the position of point *D* in Fig. 23 is so questionable that a determination of the position of *H* based on the position of *D* also is of questionable value.

The region of homogeneous gamma phase is limited below by three surfaces representing the primary separation of alpha phase, cementite, and copper. Electric-resistance-versus-temperature curves were used in locating these surfaces and their intersection. The critical points observed in a series of alloys containing 1 per cent copper and a variable carbon content are given in Table 6, and mean values are plotted in Fig. 24. The rates of heating or cooling were not stated. Line *AB* in the figure lies on the surface at which alpha iron is formed, and line *BC* lies on the

TABLE 6.—TRANSFORMATION TEMPERATURES DETERMINED BY ELECTRIC-RESISTANCE-VERSUS-TEMPERATURE CURVES*

Composition, per cent		Temperature, degrees centigrade					
		Break			Arrest point		
Carbon	Copper	Heating	Cooling	Mean	Heating	Cooling	Mean
0.55	1.29	810	780	795	740	660	700
1.00	1.00	870	820	845	730	650	690
1.18	1.00	970	925	948	735	685	710
1.24	1.24	1035	978	1005	735	665	700
1.30	1.04	1060	1005	1033	735	665	700

* Ishiwara, Yonekura,

TABLE 7.—TRANSFORMATION TEMPERATURES DETERMINED BY ELECTRIC-RESISTANCE-VERSUS-TEMPERATURE CURVES*

Composition, per cent		Temperature, °C.								
		First break			Second break			Arrest point		
C	Cu	Heating	Cooling	Mean	Heating	Cooling	Mean	Heating	Cooling	Mean
0.55	1.29	810	780	795	...	...	...	740	660	700
0.57	1.47	810	750	780	...	...	...	740	670	705
0.48	2.08	850	790	820	800	750	775	730	670	700
0.55	3.25	900	850	875	790	740	765	740	675	708
0.49	4.10	990	950	970	790	750	770	735	675	705
0.48	4.97	1020	970	995	795	745	770	740	690	715
0.54	5.80	1050	1005	1028	790	750	770	730	675	703

* Ishiwara, Yonekura, and Ishigaki.[166]

surface at which cementite is formed. Point B is on the line formed by the intersection of the two surfaces. Electric-

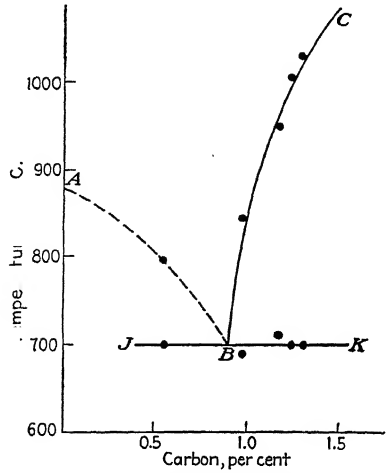


FIG. 24.—Transformation temperatures in alloys containing 1 per cent copper, determined by electric-resistance methods. (*Ishiwara, Yonekura, and Ishi-*

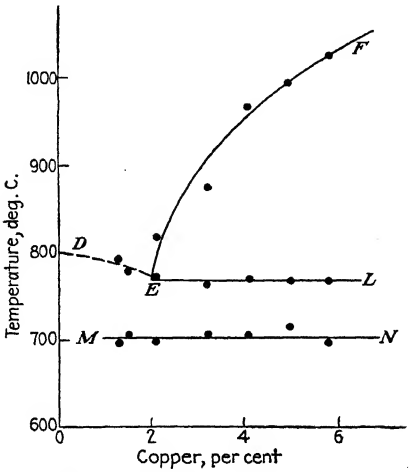


FIG. 25.—Transformation temperatures in alloys containing 0.5 per cent carbon, determined by electric-resistance methods. (*Ishiwara, Yonekura, and*

resistance-versus-temperature data for alloys containing 0.5 per cent carbon and a variable copper content are listed in Table

7, and mean values are plotted in Fig. 25. Line *DE* is on the surface along which alpha iron is precipitated; line *EF* is on the surface along which epsilon phase is precipitated, and line *MN* is along the ternary eutectoid horizontal. Arrest points in electric-resistance-versus-temperature curves for another series of alloys are shown in Table 8. Only the points observed on heating are given, because the alloys graphitized at elevated temperatures. Plotting these data indicated that the line of double saturation *HO* passed through the point 1.16 per cent carbon and 3.0 per cent copper.

TABLE 8.—TRANSFORMATION DETERMINED BY ELECTRIC-RESISTANCE-VERSUS-TEMPERATURE CURVES*

Composition, per cent		Break on heating, °C.
Carbon	Copper	
1.18	1.00	970
1.27	2.08	980
1.16	2.53	980
1.14	3.11	990
1.24	4.14	1060
1.11	4.85	1110

* Ishiwara, Yonekura, and Ishigaki.[166]

A microscopic examination of some ternary alloys indicated that the line of double saturation O_1O was parallel to the iron-copper side. Magnetic analysis indicated that its temperature fell 20°C. as the copper increased from nil to 2 per cent. The ternary eutectoid according to this study is, therefore, at a temperature of 700°C.

Expansion-temperature curves for copper-rich alloys containing 0.04, 0.36, and 0.97 per cent carbon indicated that the line of double saturation O_2O fell from 830 to 706°C. as the carbon content increased.

On the basis of their work, the Japanese investigators constructed the diagram shown in Fig. 26, which shows the lines of double saturation O_1O, O_2O, and *HO*, and isothermals for the surfaces along which iron, cementite, and copper separate from the homogeneous gamma phase. In constructing this diagram, it was assumed that the eutectoid in the iron-copper system was

at 2.33 per cent copper. As pointed out in the preceding chapter, this value appears to be low. The lines of double saturation were constructed by drawing straight lines through the points *B*, *C*, and *H*, which is a questionable procedure.

It is apparent that the data available are not adequate for determining the position of the lines of double saturation intersecting at point *O* and that point *O* cannot be definitely located.

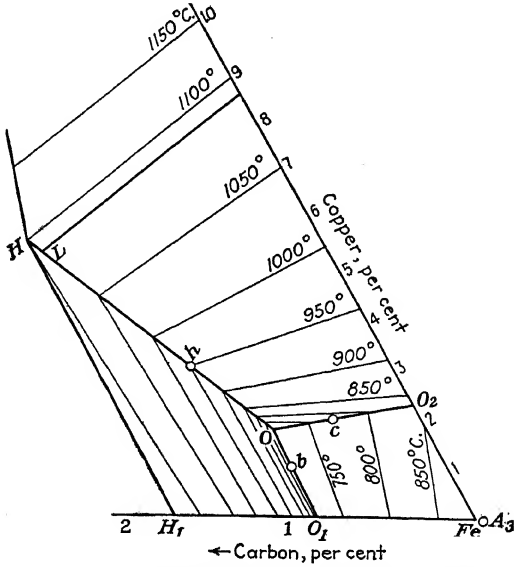


FIG. 26.—Lower surfaces of homogeneous gamma region. (*Ishiwara, Yonekura, and Ishigaki.*[166])

A number of workers have determined critical points of copper steels, but the data reported are of little help in constructing a ternary diagram. Critical-point data will be found in Chapter V.

D. AUTHORS' SUMMARY

1. A possible iron-copper-cementite diagram has been outlined by Ishiwara, Yonekura, and Ishigaki. In this diagram the two-liquid region is shown as intersecting the iron-copper liquidus, which is very probably incorrect. If the two-liquid region does not intersect the iron-copper liquidus but is separated from it by only a slight distance, the diagram should be modified,

but it may be considered as a simplification of the real diagram. In any case, the diagram is of the correct type for alloys containing even small amounts of carbon. It is consistent with the laws governing heterogeneous equilibrium and with experimental observations other than those dealing with the two-liquid region in the iron-copper system.

2. The two-liquid region covers a large part of the field. The line along which liquid, cementite, and gamma phase are in equilibrium intersects the two-liquid region. This necessitates an invariant reaction, in which the iron-rich layer is decomposed into gamma iron, cementite, and a copper-rich liquid.

3. Delta iron is stable only at high temperatures, and the delta and alpha regions do not merge.

4. Gamma phase (austenite) in the ternary system is decomposed at lower temperatures by a ternary eutectoid reaction at approximately 0.9 per cent carbon, 1.9 per cent copper, and 700°C.

5. The intersection of the two-liquid region with the liquidus on which gamma iron separates primarily has been determined and is shown in Fig. 22. This line is difficult to determine, and the line as drawn should be regarded as an approximation. Point *E* lies on this line and on somewhat questionable grounds has been stated to lie at 4.3 per cent carbon and 3 to 3.5 per cent copper. It is at a temperature of approximately 1100°C.

6. The Japanese investigators attempted to determine the lower boundaries of the homogeneous gamma field, but their location of these surfaces inspires little confidence. Their data do prove that a ternary eutectoid is present and that the invariant reaction involved occurs at a temperature approximately 20°C. below that of the eutectoid temperature in iron-carbon alloys.

7. It can, therefore, be concluded that the iron-copper-cementite diagram has been sketched, but that few if any of the significant surfaces or even lines have been accurately located. More accurate experimental data on the behavior of iron-copper-carbon alloys are needed, and a careful study of the iron-rich alloys would be a useful contribution to metallurgical science.

CHAPTER IV

MELTING AND WORKING OF COPPER IRONS AND STEELS

Smelting of Cupriferous Iron Ores—Manufacture of Copper-alloyed Wrought Iron—Manufacture of Copper Steel and Iron—Effect of Copper on Hot-working Properties of Iron and Steel—Weldability—Effect of Copper on Cold-working Properties of Steel—Effect of Copper on Pickling Action—Authors' Summary

In the earlier days of iron and steel manufacture copper acquired a bad name because it was believed by many to be harmful in the manufacturing processes and injurious to the physical properties of iron and steel; it was, therefore, considered an undesirable impurity, something to be strictly kept out of the melt. However, as a result of more recent studies of the iron-copper alloys the point of view has altered until at the present time copper is intentionally added as an alloying element in iron and steel to confer definite and desired properties.

Copper is frequently present in iron ores and pig irons. Since it is not eliminated in the iron- and steel-making processes, it accumulates in steels, and larger or smaller amounts of it are found in nearly all carbon steels. The processes of melting cupriferous ores and manufacturing copper iron and steel are essentially the same as for iron free from copper.

Copper in small amounts improves certain properties of iron and steel. Greater amounts may cause difficulties in hot working, due to surface cracking which appears in copper steels even with relatively small amounts of copper; this difficulty can, however, be obviated by proper control of forging and rolling temperatures or by the use of small additions of nickel, as recent studies have indicated.

An attempt will be made in this chapter to trace the influence of small amounts of impurities or foreign elements usually present in commercial materials on hot-working properties of copper steel and iron.

A. SMELTING OF CUPRIFEROUS IRON ORES

The smelting of cupriferous iron ores does not differ from smelting copper-free ores; all of the copper is reduced and goes into the pig.

29. Copper in Ores and Pig Irons.—The iron ores of many localities in the United States and Europe contain considerable amounts of copper. In a paper on the effect of sulphur, silicon, and copper on steel, published in 1837, Stengel[5] gave the copper content of irons and steels manufactured from ores mined in different localities in Europe. The copper content was found to range from nil to 0.44 per cent. According to an anonymous article[21] in *Chemiker Zeitung*, 1891, the copper content of some English, German, and Belgian pig irons varied from 0.016 to 0.135 per cent, and that of puddled irons from 0.01 to 0.57 per cent.

The information on the occurrence of copper in European pig irons published up to 1905, as collected by Campbell,[44] is reproduced in Table 9. It will be seen that the percentage of copper in ordinary pig irons ranges from nil to 0.14 per cent, while in one German *Spiegeleisen* the copper is given as high as 0.31 per cent, and 0.39 per cent is reported in one Russian ferrosilicon.

The copper content of pig irons made from American ores, as determined by Campbell,[44] is given in Table 10. Pig irons made from ores of the Lake Superior district were found to contain no copper, nickel, or cobalt, although the Gogebic Range is comparatively near the great copper-producing district of Lake Superior. The highest copper content reported is 0.17 per cent in pig iron made from mixed hematite and magnetite Virginia ore.

According to Campbell,[26] much iron made from Cornwall (Pennsylvania) ores contained from 0.75 to 1.0 per cent copper. The ores of Cuba are reported to give iron with about 0.10 per cent copper.

The average analysis of Sudbury (Canada) iron-copper-nickel ores, which have been used for making alloy steels, is given by Clamer[58] as follows: copper 0.8 to 2.0 per cent, nickel 2 to 5 per cent, iron 35 to 52 per cent, the remainder consisting chiefly of sulphur and gangue. In these ores the copper is usually present in the form of chalcopyrite. Colvocoresses[87] gave the

TABLE 9.—COPPER, COBALT, AND NICKEL IN EUROPEAN PIG IRONS AND FERROALLOYS*

Number	Kind of iron	Source	Copper, per cent	Cobalt and nickel, per cent
	Hematite pig	English	0.11	
	Hematite pig	English	0.10	
	Hematite pig	English	0.10	
	Forge	English	0.11	
	Mottled	English	0.10	
	Spiegeleisen	Durham, England	0.014	
	Hematite pig	Cinderford, Forest of Dean, England	Trace	
	Hematite pig	Cinderford, Forest of Dean, England	0.015	
9	Mottled pig	English	0.014	
10	Manganiferous	From Cornish ore	0.060	0.060
11	Manganiferous	From Cornish ore	0.045	0.110
12	Manganiferous	From Cornish ore	0.064	
13	Best mine pig, cold blast, from clay iron ore	South Wales		0.05
14	Mottled pig, cold blast, from clay iron ore	South Wales		0.04
15	White pig, cold blast, from clay iron ore	South Wales		0.03
16	Best mine pig, hot and cold blast, from clay iron ore	South Wales		0.07
17	White forge	Germany	0.14	
18	Gray forge	Germany	0.08	
19	Spiegeleisen	Germany	0.15	
20	Spiegeleisen	Germany	0.12	
21	Spiegeleisen	Germany	0.19	
22	Spiegeleisen	Germany	0.18	
23	Spiegeleisen	Germany	0.310	
24	Coarse-grained white pig	Eisenerz, Austria	Trace	
25	Fine-grained white pig	Eisenerz, Austria	Trace	
26	Unspecified pig	Austria	.....	Trace
27	Gray pig	Friedland, Austria	0.013	
28	White pig	Friedland, Austria	0.011	
29	Gray pig	Friedland, Austria	Trace	
30	Gray pig	Friedland, Austria		Trace Ni
31	Gray pig	Friedland, Austria		0.060 Ni
32	Low phosphorus	Hungary	0.04	
33	White pig	Alsó Sajó, Hungary	0.035	
34	Spiegeleisen	Marseilles, France	0.019	
35	Ferromanganese	Marseilles, France	0.024	
36	Ferromanganese	Marseilles, France	0.060	
37	Ferrosilicon	Marseilles, France	Trace	
38	Gray pig	Russia	0.11	
39	Ferromanganese	Russia	0.03	
40	Ferrosilicon	Russia	0.36	
41	Charcoal pig	Ural District, Russia	Trace to 0.08	
42	Ferrosilicon	Ural District, Russia	0.11	

* Campbell.[44]

average composition of Sudbury ores as 3.25 per cent nickel, 1.7 per cent copper, 40 per cent iron, 25 per cent sulphur, and 20 per cent silicon.

Analyses reported by Williams and Sullivan[383] showed that the average heat of open-hearth steel in the United States contains between 0.09 and 0.12 per cent adventitious copper.

TABLE 10.—COPPER, COBALT, AND NICKEL IN AMERICAN PIG IRONS*

Kind of ore	Source of ore	Fuel used	Composition, per cent		
			Cu	Co	Ni
Mixed limonite, carbonate, and hematite	Nova Scotia	Coke	0.011	0.012	0.015
Local hematites	Mexico	Charcoal	0.012	0.009	0.006
¾ Mesabi, ¼ Vermilion	Minnesota	Coke	Nil	Nil	Nil
Gogebic hematite	Wisconsin	Charcoal	Nil	Nil	Nil
Magnetic concentrates	New York	Charcoal	0.039	Trace	Trace
Salisbury brown hematite	Connecticut	Charcoal	0.018	0.029	Trace
⅞ local hematite; ⅛ magnetite	Virginia	Coke	0.169	Trace	0.009
Local brown hematite	Alabama	Charcoal	0.038	0.048	0.072
Native hematite and magnetite	Colorado	Coke	0.039	Nil	Nil

* Campbell.[44]

30. Recovery of Copper from Iron Ores.—Ordinarily the copper content of the ores is low so that all of the copper is dissolved in the iron and remains in the iron through all the stages of manufacture of steel or wrought iron and is concentrated in the final product.

Copper does not dissolve carbon or iron carbide to any appreciable amount and does not form any stable compounds with them.[32,43,71] It may, however, unite with sulphur or iron sulphide and form either a cuprous sulphide or a double sulphide of iron (or manganese) and copper. These sulphides may remain partly in the metal and partly be absorbed by the slag. The amount of the sulphides is naturally very small since the sulphur content is low, and, therefore, the loss in copper due to this cause is not great.

It has been alleged that copper in ore and in pig iron usually occurs with sulphur.[40,183] Experiments made by Guess[84] indicated that the presence of copper and nickel in ores does not appear to make difficult the removal of sulphur by a basic slag.

As an indication of the change in views regarding the prejudice against copper in steel a suggestion by the U. S. Geological Survey is of interest.[72] It was suggested that enormous quantities of cupriferous iron oxide resulting from the roasting of cupriferous pyrite for the manufacture of sulphuric acid might be utilized for making copper-bearing pig iron. A reviewer pointed out that this is actually done with Ducktown sinter in making pig iron for recarburizing. Much of the cast iron produced in the Birmingham district contains copper introduced from this source.

B. MANUFACTURE OF COPPER-ALLOYED WROUGHT IRON

The manufacture of copper-alloyed wrought iron presents no difficulties. The processes are essentially the same as for ordinary copper-free iron when copper-bearing ores or pig iron are used and only slightly modified when copper is added intentionally either in metallic form or as a cupriferous ore.

31. Puddling Cupriferous Pig Iron.—It was thought for a long time that copper rendered iron unfit for puddling and refining. List[7] considered that copper when present in pig iron together with sulphur is an impediment in the puddling operation. Jullien,[8] Eggertz,[10] and others stated that copper injures the welding ability of iron during puddling. This opinion prevailed for a long period of time and, aided by the fear of red-shortness thought to be caused by copper, was the reason why cupriferous iron ores were barred by iron and steel manufacturers.[12,33] It should be understood, however, that in those early times the prejudices were formed from insufficient evidence, and sometimes harmful effects have been ascribed to copper because it was the only element to be blamed, since the possible effect of other elements was not considered or was overlooked. In 1861, Schafhäutl[9] expressed the opinion that the noxious influence in the puddling process which has been attributed to copper does not exist, and that it is chiefly the state of aggregation and the metalloids mixed with the carbide of iron which exert the greatest influence.

From the results of his extensive investigation of the influence of copper on iron and steel, Lipin[33] concluded that copper, possibly up to 0.60 per cent, has no deleterious effect on puddling pig iron and that up to 3 per cent does not cause red-shortness in steel. Consequently he believed no reason to exist for barring

copper-bearing ores. Ruhfus[34] claimed that better results are obtained with open-hearth ingot iron to which 0.40 per cent of metallic copper was added than with iron with 0.3 per cent copper made directly from copper-bearing pig. Ball and Wingham[17] claimed that in the manufacture of steel a more homogeneous alloy may be obtained by introducing copper in the form of an oxide. These alleged differences are without any real proof.

32. Influence of Copper on Wrought-iron Manufacture.—The literature reveals that the question of the influence of copper on iron was considered of importance three hundred years ago. In 1627, a book was published in Paris by Louis Savot[1] in which he mentioned the difficulties which smiths experienced in working iron containing copper. Savot also referred to a still older chemist, Budelius, who stated that copper renders iron incapable of being welded. It is of interest to note that the opinions of persons acquainted with the manufacture of iron have been conflicting regarding the influence of copper. In his "Manual of Metallurgy of Iron," published in 1827, Karsten[3] described some of his experiments conducted on wrought iron in Upper Silesia to "check the conflicting opinions on the influence of copper on iron." In working pig to which 0.5 per cent copper was added the flame was light green during the whole refining process; the lump was well refined and forged well. The test was repeated with an addition of 1 per cent copper. The resulting lump iron failed to weld satisfactorily.

In 1861, Longmaid, according to Stead[39] patented in England a process for making an alloy containing from 2.5 to 10 lb. of copper per ton of iron. The copper was put into the melted cast iron and the metal then refined or puddled. Reference was made in the preceding section to the work of other investigators,[8,9,12,33] from which it may be seen that the prejudice against copper in iron was being gradually dispelled. It appears that small amounts of copper do not interfere with the puddling process and do not have an injurious effect on the quality of the resulting product. Recently several processes have been patented for manufacturing alloyed wrought irons. For example, Aston (U. S. Patent 1,492,412 of April 29, 1924) adds a small quantity of copper (or other metal) to steel as in the ordinary steel-making process, pours the molten metal into molten slag, and converts it into artificial wrought iron. Rübel

(U. S. Patent 1,033,352 of July 23, 1912) recommended adding from 1 to 3 per cent copper to iron made for dynamo sheets.

Howe,[22] having examined the contradictory evidence on the effect of copper on weldability, concluded that 0.20 per cent copper is not injurious in weld iron, but that more than 0.35 per cent copper frequently affects the welding power.

Lipin[33] investigated the effect of copper on hot workability of wrought iron by adding copper to the pig iron. The conversion of the pig into wrought iron did not present any difficulties. The chemical composition of the metal obtained was:

Element	Charge I, per cent	Charge II, per cent
Carbon	0.08	0.09
Silicon	0.08	0.09
Manganese	0.30	0.30
Phosphorus	0.089	0.054
Sulphur	0.030	0.028
Copper	0.33	0.65

His tests showed that (1) cold-bend tests were good for both metals; all specimens could be bent to 180 deg. on themselves without cracking; (2) the hot-forging tests showed no sign of red-shortness; (3) pieces of iron welded together easily, and the weld was so strong that it was not damaged by bending; (4) tensile tests gave quite satisfactory results. From these experiments Lipin concluded that several tenths of 1 per cent of copper has no deleterious effect on puddling pig iron, and that all the old ideas about the injurious effect of copper on pig iron, puddled iron, and steel are untenable.

C. MANUFACTURE OF COPPER STEEL AND IRON

In this section the manufacture of copper steels and irons by the addition of copper as an alloying element will be discussed. Such an addition does not introduce any complications in the melting and refining processes. The manufacture of copper steel or iron thus does not require special process or equipment, or variations in the operation of the open-hearth or electric furnace. The copper may be introduced as metallic copper, a ferroalloy, copper-bearing scrap, or a cupriferous ore. The additions may be made at any stage of manufacture; some

authorities recommend early additions to the charge; others prefer to add copper into the ladle.

The early literature discussed the advantages and disadvantages of various methods of making copper additions and dealt with some specific processes of making copper steel and iron. This material, chiefly of historical interest, is briefly reviewed below.

33. Manufacture of Ingot Iron and Steel from Cupriferous Ores and Pig Irons.—Campbell,[26] in 1896, stated that the iron made from the ores of Cornwall, Pennsylvania, contained from 0.75 to 1.00 per cent copper, and large quantities of rails were made from this iron alone. However, at the eastern steel works it was more often the custom to use from 25 to 50 per cent of this iron in the mixture, the rest being made from foreign ores. Large amounts of such metal were put into all kinds of steels, both hard and soft, and large quantities have been worked in puddle furnaces and in foundries.

A process was worked out for making copper-nickel steels directly from Sudbury (Canada) ores. The ores contain iron, nickel, and copper (see page 55) and have ordinarily been regarded and worked as nickel ores, all of the iron going to waste. The process treats the ore as an ore of iron and produces a copper-nickel steel directly. The process, briefly, consists of, first, desulphurizing the ores which are chiefly sulphides of iron, nickel, and copper; second, reduction smelting of the material to produce a nickel-copper pig iron; and, finally, refining of the pig iron to an alloy steel.[87,89,93,99]

34. Copper Additions.—It was suggested by Williams[36] that the introduction of small amounts of copper, such as are required for the manufacture of corrosion-resistant copper steels, may be easily effected by the use of copper-bearing ore in the blast furnace.

The use of ferroalloys was advocated by some metallurgists. It was claimed that copper alloys better with iron when introduced as ferrocopper or other ferroalloy containing copper. Willis[14] mentioned that many good manganese ores have been rejected on account of high copper content (up to 5 per cent). Such ferromanganese, however, might be used for the manufacture of copper steels.

Heusler (discussion of paper by Nehl[267]) patented a process for introducing copper into iron and steel as a manganese-copper

or a silicon-copper alloy. Schneider even patented one whereby copper is introduced in the form of a high-copper, high-carbon ferroalloy, difficult as it would be to produce a uniform composition in such an alloy (U. S. Patent 415,654 of November 19, 1889).

Copper, obviously, may be introduced into steel or iron by the use of copper-steel or iron scrap. If the quantity of copper derived from the scrap is insufficient to give the desired copper content of the metal, the remainder may be introduced by the use of metallic copper, cupriferous ore, or a cuproalloy.

The most widely used practice is to introduce the copper in the metallic state in the form of small ingots, borings, scrap, baled wire, etc.

The copper losses during the making of a heat are negligible. Losses through oxidation are probably nil; any copper oxide that may be present in the copper additions or formed during melting is immediately reduced by the carbon in the bath or by the iron. The iron will take up the oxygen and the copper oxide will be reduced even though the carbon in the molten metal is low.

Very little copper is lost by volatilization. May[210] reported that copper starts to volatilize at about 1330°C. (2425°F.). However, at this temperature all of the copper is in solution in the iron, and its vapor pressure must be very low. Therefore, there is no likelihood of any loss of copper due to this cause.

It is well known that in using alloy scrap containing chromium or manganese a considerable portion of these elements is lost in the slag. In the case of copper steel or iron all of the copper contained in the scrap will be recovered in melting.

Addition of small amounts of manganese to copper steel was alleged to be beneficial on the ground that it facilitated the dissolution of copper and insured better uniformity of steel.[96] Aluminum in small amounts was similarly claimed to be helpful in obtaining better homogeneity of copper-steel ingots.[19,23,33] Probably neither expedient is required in the case of normal additions of copper, although Wigham,[49] from his experience in making open-hearth steel for high-quality wire ropes, also concluded that copper alloys better with the steel if added in the furnace or when accompanied by a little aluminum. His trial experiments with alloying copper by adding copper pig to the ladle or to the steel as it ran into the molds were interpreted as showing that the admixture was imperfect when copper alone

was added. The results obtained were thought to be better when 0.02 per cent of aluminum was added with the copper, except when the copper exceeded 1 per cent, in which case the mixture was considered imperfect. Adding copper to the charge and working it down with the steel in the furnace produced excellent results. Wigham concluded that more copper could be employed, provided it was in the metal before the heat of steel was finished. Apparently, problems of homogeneity and of deoxidation were intertwined in these experiments.

Clevenger and Ray,[70] in making copper steel by the crucible process, prefer to kill the metal thoroughly before adding the copper; hence they advise adding a small quantity of some deoxidizer, such as aluminum, just before pouring. They made crucible-steel ingots containing up to 5 per cent copper with 0.4 to 0.6 per cent carbon and 0.30 to 0.45 per cent manganese.

According to Kinnear,[291] in the manufacture of electric steel for castings the copper may be added either to the ladle or to the bath, but preferably to the bath after the slag is thinned out. However, he remarked that when this addition was made to the bath a slight drop in carbon was noted, which may have been caused by the oxides introduced with the copper.

35. The Rôle of Oxygen in the Manufacture of Copper Steels. Oxygen in small amounts is found in all commercial iron and steel and is generally considered a harmful impurity. It has been suggested[40,41] that the amount of copper permissible in open-hearth or Bessemer steel or iron without producing "red-shortness," which early observers ascribed to copper, is of variable amount, depending on the composition of steel and the amount of oxygen dissolved in it, the degree to which it has been subjected to an oxidizing influence, and the degree to which the oxides have been eliminated from the steel.

The better quality claimed for copper steels and irons made from Swedish pig has been attributed to its purity and particularly to its freedom from oxygen. Discussing the dependence of the quality of steel on the chemical characteristics of the charge, Genzmer[37] stated that a charge consisting of Swedish pig iron and ordinary scrap can take a higher percentage of copper without the appearance of what he termed "red-shortness." Steels made from German pig iron and scrap were said to behave quite differently. Small amounts of copper added to such a heat were thought to produce decided red-shortness, and this

difference was attributed to the pig iron used. The Swedish iron was quite free from oxygen compounds, while ordinary German pig contained impurities in the form of oxides.

The statements of various investigators reviewed above do not allow drawing any definite conclusions about the proper time for making copper additions. The question still remains open whether the copper additions should be made before or after the deoxidizing agents are introduced, though it is probable that the time at which the addition is made is of little actual importance.

36. The Rôle of Sulphur.—Sulphur is another element whose rôle in the process of manufacturing copper steels and irons is not thoroughly understood. It has been claimed that if the sulphur content is above the accepted maximum, red-shortness appears at lower copper contents than when the sulphur is low. Genzmer[37] stated that, if sulphur and phosphorus are above the accepted limits, the red-shortness shows with the copper content as low as 0.20 per cent. Ruhfus[34] placed the minimum copper content at 0.30 per cent. Genzmer also claimed that iron to be used for stamping should not contain above 0.25 per cent copper, even if the sulphur and phosphorus are low.

A desulphurizing effect of copper has been reported by several investigators. Clevenger and Ray[70] found that their steels decreased considerably in sulphur as the percentage of copper increased. A copper-free steel contained 0.039 per cent sulphur. When this steel was alloyed with 4 or 5 per cent copper, the sulphur content decreased to 0.020 per cent. Breuil[50] found a similar drop in sulphur, from 0.017 to 0.011 per cent. Several other investigators reported similar observations, but the evidence is not positively convincing, and further investigation is needed.

Iron and sulphide of iron (FeS) are mutually soluble in all proportions in the liquid state. In his investigation of copper mattes (Fe-Cu-S system) Bogitch[161] showed that the addition of 3 per cent copper to such solutions produces strong segregation. When the copper content exceeds 3 per cent the alloy separates into two liquid layers of very different densities and compositions, the upper layer being rich in sulphur and the lower containing only a few per cent of sulphur.

This indicates that copper decreases the solubility of iron sulphide in iron. It may be possible that copper, when added to

a metal bath in the furnace, will drive the iron sulphide out of solution. It seems probable that the reaction just described will cause partial desulphurization of the steel.

On the other hand, it has been claimed that copper prevents desulphurization of iron by manganese in the iron mixer. Guertler and Meissner[115] interpreted their experiments as showing that this undesirable effect is not caused by the formation of Cu_2S and postulated that copper increases the solubility of MnS in iron in the fluid state. Microscopic and thermal analyses of ternary copper-manganese-sulphur alloys led to the conclusion that the affinity of manganese for sulphur is higher than that of copper. In order to reconcile this finding with the fact that the presence of copper in the iron mixer prevents desulphurization by manganese, the authors microscopically investigated melts of the following composition

	Percentage
Copper	59.37
Sulphur	14.98
Manganese	25.65

to which enough iron was added so that the alloys might consist of either Cu_2S and solid solution of equal parts of iron and manganese, or MnS and two distinct layers of copper and iron.

Under the microscope the alloys showed three layers: the top layer of MnS, the iron layer, and the copper layer. The iron layer consisted of the following constituents: primary iron dendrites, Fe-MnS eutectic, gamma-iron eutectoid, and emulsified copper inclusions. The copper layer contained primary precipitations of MnS, but no eutectic MnS; it also contained beadlike iron inclusions, as well as some dendritic iron.

37. Phosphorus in Copper Steels and Irons.—It has been claimed that increasing the phosphorus content of copper steels results in considerable improvement in tensile properties. Several processes developed at Vereinigte Stahlwerke have been patented, and it was claimed that the addition of phosphorus to copper steels in such amounts as to bring its content up to 0.20 per cent or sometimes even as high as 1 per cent considerably raises the tensile strength and the elastic limit (British Patents 370,064 of April 7, 1932, and 373,640 of May 17, 1932), increases the resistance to wear (French Patent 720,035 of February 15, 1932), and increases the corrosion resistance of copper steels and

their resistance to oxidation at elevated temperatures (British Patent 365,538 of January 18, 1932).

On the other hand, it has been claimed that the cold-shortness due to excessive amounts of phosphorus can be obviated by adding small amounts of copper (0.15 per cent) to the iron or steel in the process of manufacture [British Patents 373,640 of May 17, 1932, and 377,153 of January 12, 1931 (void)], and that copper decreases greatly the rate of solution in acid of steels which had been made easily soluble by high-phosphorus or sulphur content.[312] Smith and Palmer,[378] however, found that copper accentuates rather than removes the lower impact resistance due to phosphorus, even in the low-carbon steels. Unpublished work by Lorig and MacLaren is in line with Smith and Palmer's findings.

A process has been patented whereby the desired phosphorus content is produced wholly or partly by means of reagents which reduce the phosphorus from the slag. In the manufacture of high-phosphorus steels a thorough deoxidation is considered necessary. Deoxidizers, such as ferrosilicon, aluminum, and silicoaluminum, which reduce the phosphorus from the slag, are recommended [British Patent 377,167 of January 14, 1931 (void)].

While a beneficial effect of phosphorus in copper steels has been emphatically claimed, no explanation has yet been advanced regarding the mechanism of this effect, and no technical publications giving actual data to support the claims have appeared.*

38. Ingot Casting.—No mention of any difficulties in making copper-steel ingots is found in modern literature, although enormous amounts of copper steel have been successfully made. This may be taken as an evidence that the addition of small amounts of copper to steel does not introduce difficulties in producing sound ingots. Pouring and casting copper steel or iron does not present anything unusual, except perhaps the green flame coming out of the molds or visible around copper-steel ingots in the soaking pit. It has been noted that the effect of copper on pig iron is not so great as that of other elements. Addition of copper does not seem to exert any great effect on

* In reviewing the manuscript, E. H. Schulz of Vereinigte Stahlwerke, A.-G., wrote that recent work of his associate Carius has proved that a high phosphorus content improves the corrosion resistance of copper steel and reasons for this improvement have been found. The results of the investigation will be published within the next few months (letter of May 24, 1934).

the fluidity of pig iron, although it has been reported that the fluidity of Swedish pig iron increases with rising copper content.[33] A copper content above 10 per cent seems to render pig iron somewhat sluggish.[132]

The *Fourth Report on the Heterogeneity of Steel Ingots*[321] stated that copper seems to have a quieting effect on steel poured into ingots. Lorig and MacLaren* also noticed the same effect in the case of cast steels. While steel without copper was decidedly gassy, the addition of 0.6, 1.2, and 1.7 per cent copper was increasingly effective in quieting the steel. The steel with 1.7 per cent copper taken from the same heat from which copper-free test blocks were poured was absolutely sound, while the copper-free steel was worthless because of blow holes.

Copper does not cause surface defects in iron or steel ingots. Kinnear[291] observed that shrinkage cracks are encountered to no greater extent in copper steel than in any other steel. He concluded from his experience that there are fewer cold checks in copper steel than in any other steel.

To prevent liquation or segregation in steels containing appreciable amounts of copper, rapid solidification of ingots by pouring at low temperatures and by the use of heavy chill was recommended.[96]

39. Segregation.—It is obvious that when copper is present in an alloy greatly in excess of the amount that can be dissolved by the iron the two metals will segregate. Examples of this segregation have been given in Chapter II. The high-copper alloys, however, do not appear to be at present of practical importance; of greater interest are the alloys containing copper in quantities which can be held in solution by iron in the solid state. When such an alloy is cast into a mold, the iron-rich phase freezes out first, enriching the remaining molten metal in copper, as may be seen from the iron-copper equilibrium diagram. The data available on the segregation of copper in the iron-rich alloys refer mainly to copper steels.

The only investigation on segregation of copper in relatively pure iron-copper alloys appears to be that made by Burgess and Aston.[53] Their alloys, which were cast as 1-lb. ingots, contained up to 7 per cent copper, the total amount of impurities being less than 0.10 per cent. From a series of analyses on

* Unpublished work.

random forgings (bars) they concluded that the alloys investigated were entirely free from segregation.

It has also been found that copper segregates but little in steel and in pig and cast iron. Colby's[31] investigation of large open-hearth steel ingots containing 0.59 per cent copper showed that the copper segregation was insignificant. The highest copper found in the ingot was 0.61 per cent in drillings showing twice as much sulphur and phosphorus as the ladle test contained. This seems significant as opposed to the claim that copper is present in combination with the sulphur.

Breuil[50] studied the segregation of copper in three sets of small (110-lb.) experimental ingots with copper content varying from nil to 32 per cent, the carbon being 0.10 to 0.16, 0.28 to 0.41, and 0.56 to 0.80 per cent in the three sets of ingots. Chemical analyses showed no marked segregation in the ingots containing less than 4 per cent copper regardless of the carbon content. With higher copper content the segregation was the more pronounced the higher the carbon. These observations were in general confirmed by hardness tests taken on longitudinal sections of the ingots. Clevenger and Ray[70] noted some slight segregation in small ingots when the copper content was increased to 0.85 per cent. In a steel with 4.5 per cent copper and 0.46 per cent carbon the segregation became very marked.

The size of ingots apparently does not affect the segregation of the copper when only small percentages are present. Wüst and Felser[65] analyzed comparatively large (1000-kg.) and small (340-kg.) ingots of open-hearth steel containing 0.35 per cent copper and found virtually the same degree of segregation in both sizes of ingots, the copper segregation being apparently independent of the rate of cooling. Sulphur was found to segregate more in large ingots—phosphorus, manganese, and carbon more in small ingots. Some average analyses taken on longitudinal sections of ingots presented in Table 11 give an idea of the degree of segregation of copper as compared with segregation of other elements.

An extensive investigation on segregation in low-copper steels was made by Bardenheuer and Müller.[225,226] The investigation comprised all common elements usually found in steels and their mutual effect on segregation. Some attention was given to the influence of deoxidation on segregation. Tests were made on small ingots (50-kg.) and also on large commercial ingots. The

TABLE 11.—AVERAGE ANALYSES ON LONGITUDINAL SECTIONS OF OPEN-HEARTH STEEL INGOTS*

Element	Large ingots			Small ingots		
	Composition, per cent		Segregation, per cent†	Composition, per cent		Segregation, per cent†
	Rim	Core		Rim	Core	
Carbon.....	0.079	0.079	0.0	0.066	0.083	26.0
Phosphorus.	0.052	0.103	100.0	0.044	0.080	82.0
Sulphur.....	0.037	0.106	190.0	0.037	0.092	150.0
Manganese.	0.038	0.400	5.3	0.421	0.466	11.0
Copper.....	0.303	0.377	24.4	0.300	0.373	24.0

* Wüst and Felser.[65]
† Average percentage deviation between minimum and maximum values.

TABLE 12.—COMPOSITION OF STEEL INGOTS*

Ingot	Composition, per cent								
	C	Mn	Si	P	S	Cu	O	N	Al
1	0.06	0.32	Trace	0.034	0.047	0.08	0.027		
2	0.01	0.03	Trace	0.006	0.107	0.15	0.113	0.0078	
3	0.03	0.10	Trace	0.011	0.201	0.44	0.050	0.0075	
4	0.08	0.11	Trace	0.008	0.229	....	0.075	0.0087	
5	0.07	0.20	Trace	0.069	0.037	0.19	0.002	0.0164	
6	0.02	0.14	Trace	0.090	0.059	0.17	0.063	0.0085	
7	0.02	0.20	Trace	0.257	0.035	0.11	0.032	0.0075	
8	0.05	0.10	Trace	0.289	0.196	0.23	0.070	0.0071	
11	0.01	0.14	1.68	0.029	0.042	0.10	.....	0.0045	
12	0.03	0.09	0.87	0.010	0.187	0.21	0.018	0.0081	
I	0.09	0.43	Trace	0.054	0.087	0.21			
II	0.09	0.49	Trace	0.059	0.069	0.20	.....	.....	0.05
III	0.10	0.39	Trace	0.024	0.049	0.24			

* Bardenheuer and Müller.[225]

copper content varied from 0.08 to 0.44 per cent. The compositions of some of the ingots investigated are shown in Table 12.

The ingots were split longitudinally, and tests were made along the center line and near the surface. Some of the results are shown in Figs. 27, 28, and 29, where the positions of the tests in the ingots are designated by Roman numerals, I to IX,

starting from the top. It may be observed that segregation is very slight, the copper concentration increasing slightly toward the center line and the middle of the ingot. Examination of the curves shows that copper segregates with the sulphur, although to a much smaller degree The mean segregation expressed in percentage deviation between surface and core for

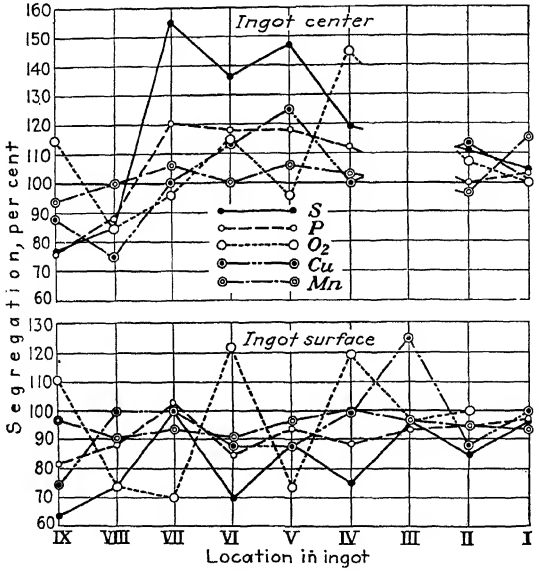


FIG. 27.—Segregation in copper-steel ingot 1. (*Bardenheuer and Müller.*[225])

ingots 1 to 8, taking the ingot analysis as 100 per cent, is given below:

Element	Ingot number								Average of 8 ingots
Copper.....	6	18	7				18		10
Sulphur....	35	106	68	38	37	69	66	68	60
Phosphorus.	12				17	53	50	35	35
Manganese.					7	6			7
Oxygen.....	11	24	16	27		16		11	16

It may be seen that copper segregates only to a slightly greater degree than manganese and much less than phosphorus or sulphur.

40. Effect of Deoxidation on Segregation.—The results obtained by Bardenheuer and Müller also indicate that segregation, in general, decreases with more complete deoxidation. In Fig. 30 the segregation of manganese, phosphorus, sulphur, and copper is plotted against the oxygen content. One will observe that with increasing oxygen the copper segregation increases

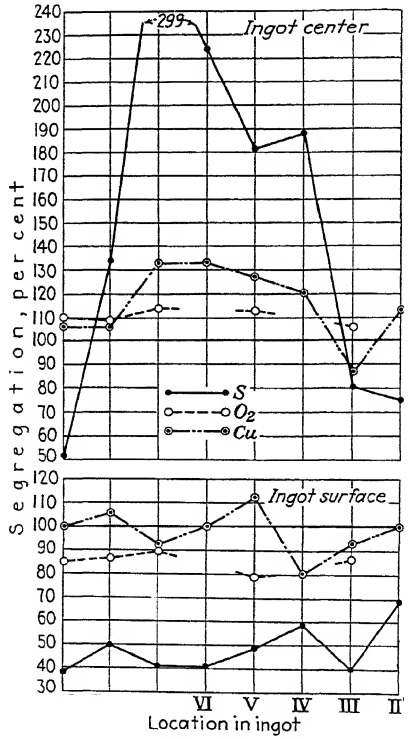


FIG. 28.—Segregation in copper-steel ingot 2. (*Bardenheuer and Müller.*[225])

but slightly, the maximum deviation from the ingot analysis being 18 per cent when the oxygen content attains the value of 0.11 per cent. Neither killed nor rimmed steels show much copper segregation. An example of segregation of copper and other elements in killed steel is given in Fig. 31.

The effect of deoxidation is shown still more strikingly in Fig. 32, representing the percentage deviation of various elements from ingot analysis obtained on large basic open-hearth steel

ingots. Ingot II was killed with 0.15 per cent aluminum. The rimming ingots I and III show greater segregation of manganese, phosphorus, and sulphur than ingot II; greater segregation in ingot I as compared with ingot III is due to the higher oxygen content of ingot I.

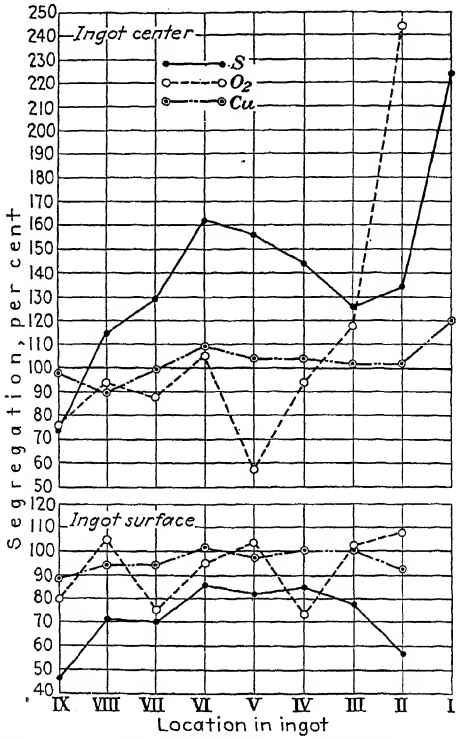


FIG. 29.—Segregation in copper-steel ingot 3. (*Bardenheuer and Müller.*[225])

The Committee on the Heterogeneity of Steel Ingots[321] reported that copper in steel exhibits considerable tendency to segregate, the segregation being smaller the higher the copper content. The committee found that copper with respect to segregation occupies an intermediate position among other elements; sulphur, phosphorus, and carbon show the greatest tendency to segregate; silicon, manganese, nickel, chromium, titanium, and aluminum segregate very little, while copper and

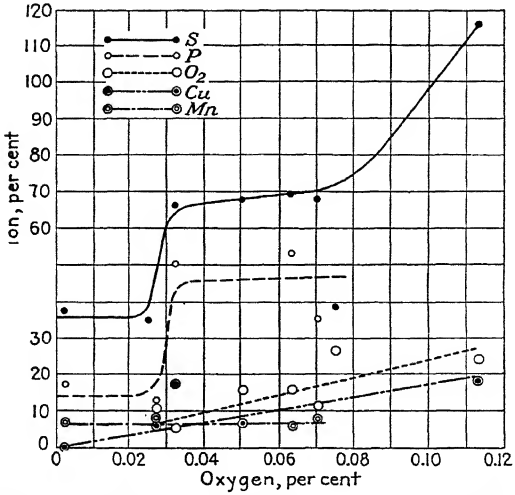


FIG. 30.—Effect of deoxidation on segregation in copper-steel ingots. (*Bardenheuer and Müller.*[225])

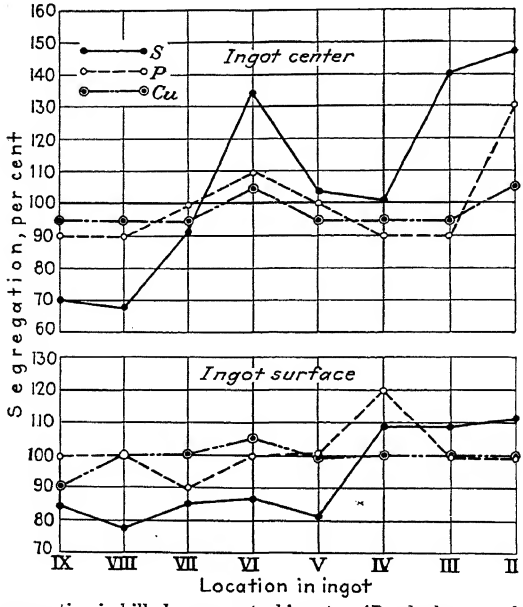


FIG. 31.—Segregation in killed copper-steel ingot. (*Bardenheuer and Müller.*[225])

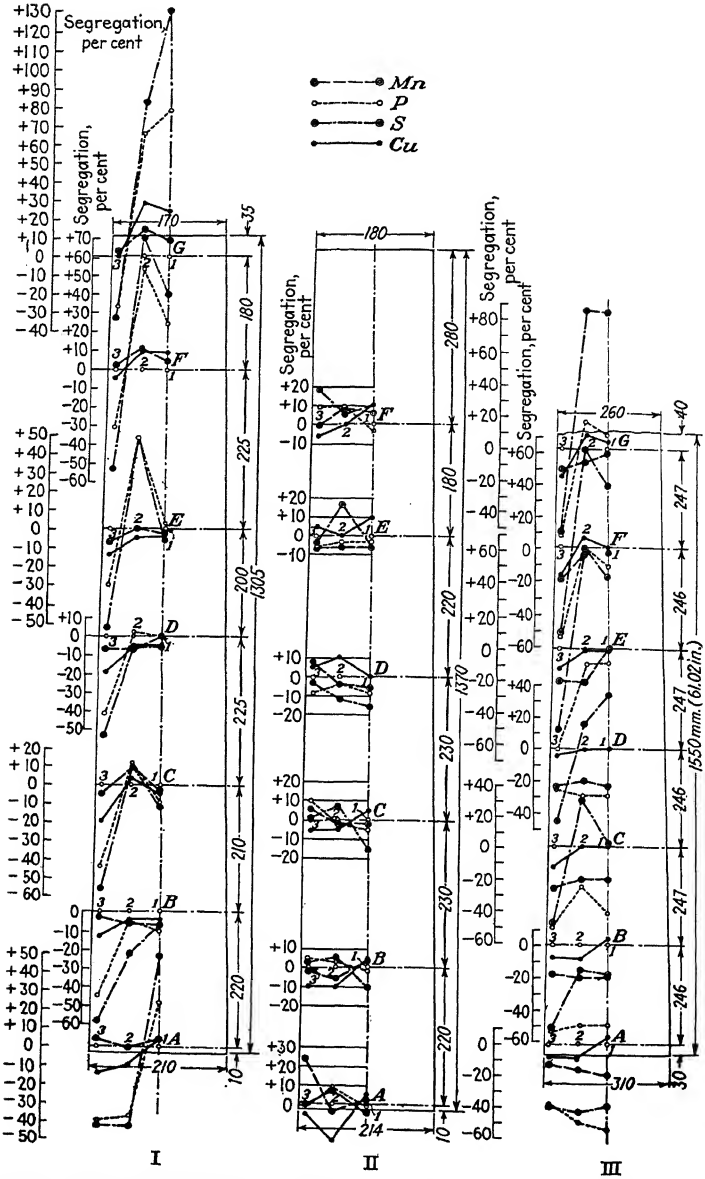


FIG. 32.—Effect of deoxidation on segregation in large steel ingots. (*Bardenheuer and Müller.*[226])

arsenic occupy the intermediate position between these two groups.

D. EFFECT OF COPPER ON HOT-WORKING PROPERTIES OF IRON AND STEEL

From the earliest times an effect of copper in producing cracking of iron and steel during hot working has been noted, but the various investigators disagreed about the amount of copper required to produce the effect, several failing to find it.

The reason for the discrepancies lies in the failure to note the different behavior of the same material at different temperatures of heating and working and the disregard for the effect of other elements present in the materials. Another reason for discrepancies lies in the fact that some of the early observers did not discriminate between true red-shortness and surface cracking in steel.

Commercial copper steels with copper content not exceeding 4 per cent are free from true red-shortness. Surface cracking, however, may occur in steels with the copper content as low as 0.20 per cent. In commercial experience with steels containing between 0.20 and 0.30 per cent copper, slight edge cracking is noted, not of a very serious nature but nevertheless clear enough so that copper-bearing billets can be separated in the mill from other billets by examination of the edges.

Recent work indicated that both red-shortness and surface cracking, although distinct, may be traced to the low melting point of copper. Bodily red-shortness in high-copper alloys, extending through the metal, is caused by the intergranular films of copper-rich constituent melting at 1094°C. (2000°F.). Surface cracking was found to be caused by preferential oxidation of iron during heating, which leaves metallic copper under the scale. If working is done above the melting point of this copper-rich deposit, the copper penetrates into the steel and thus weakens the intergranular cohesion.

In steels with an abnormally low manganese-sulphur ratio intergranular films of copper sulphide might occur and produce red-shortness, but there is no evidence of such films in ordinary copper steels.

Recent work indicated that surface roughening of copper steels may be entirely eliminated by the addition of a small amount of nickel or possibly cobalt.

Various observations and theories on red-shortness are briefly summarized below.

41. Some Observations on Forgeability of Iron-copper Alloys. A great deal has been said and published on the effect of copper on hot workability of iron and steel. Most of the early reports are, however, unreliable for the reasons mentioned above and are, therefore, omitted in this review. The general consensus of opinion seems to be that copper if present above certain amounts causes so-called red-shortness, which, however, may be modified by other elements present in the alloy.

Howe[22] in summarizing the information available in the literature up to 1890 gave the following properties of alloys of carbonless iron and copper:

Copper, per cent	Properties
2	Red-short, weak when cold
9	Hard and brittle
16.7	Stronger than the 2 per cent and the 9 per cent
20	Very brittle, crystalline, granular
25	Segregated, bottom soft malleable copper
41.75	Very brittle, fracture uneven
50	Very brittle and fine-grained
80	Less ductile than pure copper
83.4	Red-short, harder and tougher than copper
94	Very ductile, stronger than copper
94	Harder than copper, magnetic

The first systematic investigation of the properties of relatively pure iron-copper alloys was made by Burgess and Aston.[53,57] Alloys of varying copper content were melted from doubly refined electrolytic iron and electrolytic copper. One-pound ingots were prepared and forged into 0.625-in. rounds. The forged bars analyzed 0.047 per cent carbon, 0.005 per cent sulphur, 0.062 per cent silicon, and 0.016 per cent phosphorus. The following characteristics were noted during the forging: Alloys containing up to 2 per cent copper forged well and at low temperatures. Alloys with 2 to 7 per cent copper could not be forged at low temperatures and forged poorly at a white heat. With 7 to 80 per cent copper the alloys could not be forged. With 80 to 100 per cent copper they forged at fair red heat but not at normal forging temperatures for iron. In earlier work alloys above 5 per cent copper could not be worked; in later tests alloys with 5 and 10 per cent copper were tried at all temperatures, and it was found that with care and at a high

temperature (welding) a 7 per cent alloy could be forged. An 80 per cent copper alloy forged cold and could be worked well at dull red heat, but a 75 per cent copper alloy broke. The high-copper alloys (90 per cent copper and above) could not be forged when 1 per cent of silicon was present.

All the observations may be summarized as follows:

1. Alloys containing less than 2 per cent copper forge well.
2. Alloys containing 2 to 7 per cent copper do not forge at red heat, and poorly at white heat.
3. Alloys containing 7 to 80 per cent copper are non-forgeable.
4. Alloys containing 80 to 100 per cent copper forge at fair red heat.

The results of Burgess and Aston were, in general, confirmed by Ruer and Fick.[73] In preparing the specimens for their study of the iron-copper diagram the latter workers observed that alloys with 6 to 80 per cent copper could not be forged; other alloys were forged into the desired shape.

The results of Smith's* tests for forgeability at low but undetermined temperatures represented in Table 13 indicated that with minor exceptions alloys containing up to 8 per cent copper are forgeable. This limit is a little higher than previous investigators have found, Burgess and Aston regarding 7 per cent as the limit. The 8.6 and 9.3 per cent alloys were unforgeable. Attention is called to the somewhat higher silicon and manganese contents of Smith's alloys as compared with those of Burgess and Aston and to the heat treatment the alloys had received.

Hot-working properties of pure iron-copper alloys were also investigated by Richardson and Richardson.[118] Their alloys were prepared by melting commercially pure iron in an electric furnace and adding copper to the molten iron. The forging tests were made by heating the ingots to a bright-red heat and then forging continuously to a black heat, the operation being repeated until the desired shape and size were obtained. They noted that very small amounts of copper make the alloy brittle in forging, but that the brittleness appears only in a certain temperature range. Below and above this range the metal was forgeable. Furthermore, they found that the degree of brittleness and the temperature range over which it occurs increased with the increase in copper content.

Cain[139] noted that bars of iron-copper alloys which could be forged throughout the brittle range without breaking or serious

* Private communication by C. S. Smith of American Brass Company.

TABLE 13.—ANALYSES AND FORGING CHARACTERISTICS OF IRON-COPPER ALLOYS*

Alloy number	Composition, per cent				Rockwell *C* hardness, normalized†	Forgeability
	Cu	Mn	Si			
489	1.08	0.050	0.149	0.024	-22.3	Forgeable‡
490	2.05	...	0.079	.....	- 9.8	Forgeable‡
491	2.83	0.049	0.140	0.027	2.3	Forgeable‡
492	3.56	...	0.079	...	3.6	Forgeable‡
493	4.23	0.041	0.062	0.026	4.6	Badly quench-cracked. Probably forgeable if sound‡
494	5.94	0.041	0.074	0.030	5.6	Forgeable‡
495	6.79		0.091		3.4	Forgeable‡
496	7.74		0.058		6.2	Forgeable, save where quench-cracked‡
497	8.57	0.036	0.065	0.024	7.2	Unforgeable‡
498	9.33		0.054		4.2	Unforgeable‡
657	1.10		0.192			Forgeable
660	2.13		0.154			Forgeable
663	3.04		0.114			Forgeable

* C. S. Smith, American Brass Company.

† Forged rods normalized at 900°C. (1650°F.) for 1 hr., air cooled.

‡ Received preliminary homogeneizing anneal [16 hr. at 950°C. (1740°F.) followed by quenching] prior to forging.

cracking were red-short in a bend test. Stead and Evans[38] reported that in one of their experiments 0.5 per cent of copper added to an open-hearth steel, instead of producing red-shortness, changed a red-short carbon steel into a steel which could be rolled without cracking.

42. Effect of Copper on Forging and Rolling of Steel.—Early attempts to determine the amount of copper which can be alloyed with steel without producing red-shortness yielded very divergent results. The maximum permissible copper content was stated to be from 0.3 to 4.5 per cent.[13,15,16,17,34,38,50] According to Clevenger and Ray,[70] in forging crucible-steel ingots containing 0.50 to 0.60 per cent carbon traces of red-shortness begin to appear with a copper content of 4.5 per cent.

No definite conclusion can be drawn from these observations, because in most cases the testing conditions were not specified. An investigation of Lipin[33] indicated that the behavior of copper steels in hot-working operations depends not only on the copper content but also on the temperature of working and on the

carbon content. It was found that experimental low-carbon steels (0.10 per cent carbon) could be forged at temperatures between 900 and 930°C. (1650 and 1705°F.) without any trouble as the copper content was increased to about 3 per cent. Steels with larger amounts of copper showed surface cracking; with 7 to 10 per cent copper the steels could not be forged and fell

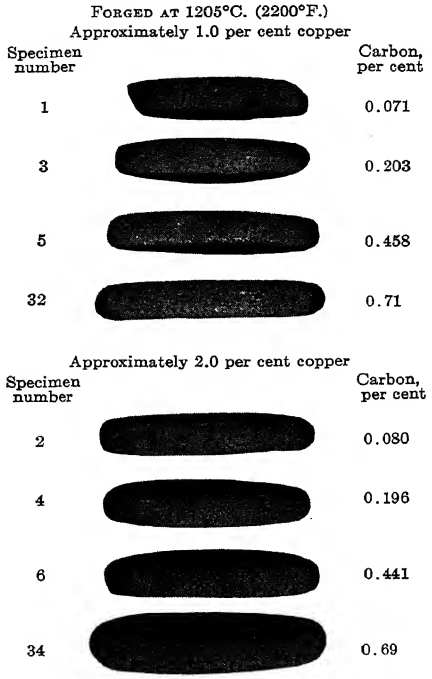


Fig. 33.—Roughened edges of forged copper-carbon steels showing the effect of copper and carbon contents. (*Lorig and MacLaren.*)

to pieces. Medium-carbon steel (0.4 to 0.45 per cent) rolled well with copper content up to 2 per cent. The steels with a higher copper content required heating at higher temperatures whereby surface cracks occurred, indicating that as the carbon content increased the copper content had to be lowered in order to avoid cracking. In the notched-bar bending test for red-shortness the steels with 0.5 per cent carbon showed only traces of red-shortness when the copper content exceeded 1 per cent Specimens with 4 per cent copper were decidedly red-short.

As has been shown in Chapter II, Ishiwara, Yonekura, and Ishigaki found that the amount of copper required to produce the epsilon phase decreases with increasing carbon content. This means that red-shortness would be observed at lower copper contents as the carbon content increases.

43. Effect of Carbon Content on Red-shortness and Surface Cracking.—The effect of carbon content on hot workability of

FIG. 34.—Steel containing 1.03 per cent copper and 0.07 per cent carbon, forged at 1205°C. (2200°F.). Unetched. 50×. (*Lorig and MacLaren.*)

copper steels was also studied by Lorig and MacLaren.* The effect of carbon on surface cracking of copper steels is shown in Fig. 33 illustrating the appearance of forged test specimens of 1.0 and 2.0 per cent copper steels with varying carbon. It will be seen that in both sets of specimens the surface cracks are deeper the higher the carbon content. The average depth of penetration in millimeters for specimens 1, 32, and 34 is given below:

Specimen	Composition, per cent		Average penetration, mm.
	Copper	Carbon	
1	1.03	0.07	0.30
32	1.07	0.71	0.56
34	1.77	0.69	0.90

* Data from these workers, obtained at Battelle Memorial Institute on work sponsored by the Copper and Brass Research Association, are included here and on later pages through the courtesy of the association.

The effect of carbon and copper on the nature and the extent of cracks is also shown in Figs. 33 to 36. These photographs were

FIG. 35.—Steel containing 1.07 per cent copper and 0.71 per cent carbon, forged at 1205°C. (2200°F.). Unetched. 50×. (*Lorig and MacLaren.*)

taken of polished surfaces normal to the roughened faces of the disks forged at 1205°C. (2200°F.).

FIG. 36.—Steel containing 1.77 per cent copper and 0.69 per cent carbon, forged at 1205°C. (2200°F.). Unetched. 50×. (*Lorig and MacLaren.*)

44. Effect of Other Elements.—The elements manganese, chromium, sulphur, and oxygen are mentioned frequently in the literature as affecting the hot workability of copper steel.

The first two are referred to as beneficial and the latter two as injurious.

The effect of oxygen and sulphur on the steel-manufacturing processes was considered earlier in the chapter. It was mentioned that both of these elements impede the puddling process and tend to render iron and steel red-short.

Manganese was claimed by a number of investigators to be beneficial in reducing red-shortness in copper steels.[35,79,96,105] Its effect might be due to several reasons: (*a*) It may increase the solubility of copper in iron; (*b*) it deoxidizes steel and, therefore, reduces the segregation of copper which may be responsible for the red-shortness; (*c*) it keeps the sulphur in solution or forms a sulphide (MnS). In order to be effective manganese should be present in amounts sufficient to make the manganese-sulphur ratio sufficiently high. Experiments of Cain[139] indicated that manganese may prevent red-shortness in iron when present to the extent of three times the sulphur content, if the oxygen content is not above 0.04 per cent.

45. Investigation of Lorig and MacLaren.—A series of steels was made to contain 0.60 to 0.70 per cent manganese, 0.50 and 0.70 per cent carbon, 0.15 per cent silicon, and 1.0, 1.5, and 2.0 per cent copper. Heats were made in an electric furnace and poured into 55-lb. ingots. The test for red-shortness consisted in forging these ingots (3.5-in. octagonals) to 1-in. rounds. Forging was done at 1205°C. (2200°F.) maximum temperature, the variation between ingot temperatures being some 150°C.

TABLE 14.—CHEMICAL COMPOSITIONS OF COPPER STEELS*

Steel number	Composition, per cent†		
	C	Cu	Cr
33	0.30	0.20	
34	0.30	0.40	
35	0.30	0.60	
36	0.30	0.80	
37	0.70	0.20	
38	0.70	0.40	
39	0.70	0.65	
40	0.70	0.80	
41	0.30	1.00	0.10

* Lorig and MacLaren.

† Also contained 0.70 per cent manganese and 0.15 per cent silicon.

(300°F.). All the steels forged well, and no difference was observed between the copper-bearing and copper-free steels. However, on some of the copper-steel bars a network pattern was observed consisting of fine surface cracks extending to a depth of about 1/16 in. To determine the minimum amount of copper at which surface roughening occurs a series of alloys was prepared; compositions are given in Table 14.

The steels were forged after soaking 1 hr. at 1095, 1150, 1205, and 1260°C. (2000, 2100, 2200, and 2300°F.). Faint traces of surface cracking were observed in the specimens containing 0.20 per cent copper; the roughening increased progressively with increasing copper content.

The average penetration of surface cracks in a steel containing 0.70 per cent carbon and 0.20 to 0.80 per cent copper, forged at 1150 and 1205°C. (2100 and 2200°F.), is shown below:

Specimen number	Forging temperature		Composition, per cent		Average penetration, mm.
	°C.	°F.	C	Cu	
37	1150	2100	0.70	0.20	0.077
38	1150	2100	0.70	0.40	0.194
39	1150	2100	0.70	0.60	0.276
40	1150	2100	0.70	0.80	0.366
37	1205	2200	0.70	0.20	0.055
38	1205	2200	0.70	0.40	0.200
39	1205	2200	0.70	0.60	0.351
40	1205	2200	0.70	0.80	0.401

It is apparent that the depth of penetration at a given temperature increases almost linearly with the copper content.

In order to establish accurately the temperatures at which surface cracking occurs in forging copper steels, Lorig and MacLaren tested a series of steels with carbon varying from 0.50 to 0.70 per cent and copper from 0.07 to 2.06 per cent. The tests were conducted on small cylindrical specimens machined to 0.75-in. diameter and 1.5-in. length. The cylinders were heated to the required temperatures, quickly withdrawn from the furnace, and flattened into disks about 0.25 in. in thickness by means of a few sharp blows of an air hammer. Examination of the edges of the disks served as a criterion in judging the forging properties of the material.

Tests made at temperatures between 760 and 1260°C. (1400 and 2300°F.) showed that surface cracking appears in all specimens forged above 1065°C. (1950°F.). At temperatures near 1065°C. (1950°F.) roughening was hardly perceptible, but above this temperature the intensity of the roughening became more

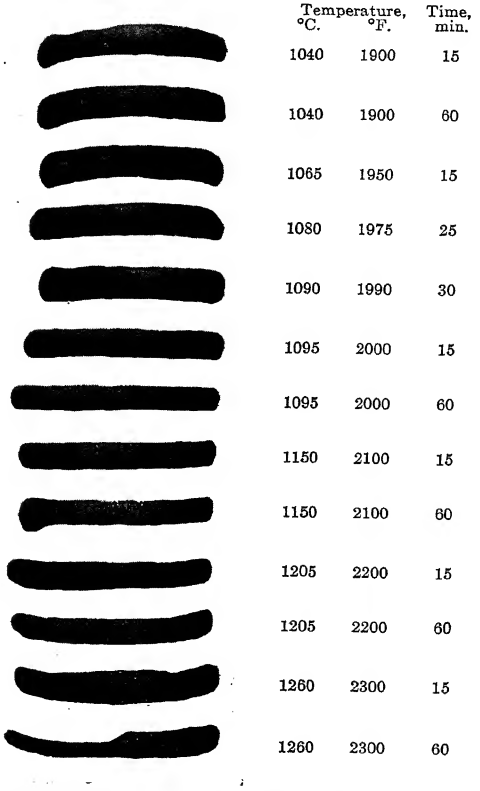


FIG. 37.—Effect of heating temperature and time on surface roughening in copper-bearing steels. (*Lorig and MacLaren.*)

and more pronounced the higher the forging temperature and the longer the heating time. The appearance of one series of specimens of approximately the same copper content is shown in Fig. 37.

From the observations reviewed above, the following conclusions regarding the effect of copper on hot-working properties of steel may be drawn:

1. The higher the carbon content, the lower the amount of copper that can be alloyed without causing forging difficulties.
2. The intensity of surface roughening increases with increasing temperature, with time of heating, and with the copper content of the steel.
3. No perceptible surface roughening takes place at any temperature if the copper content does not exceed 0.20 per cent, nor does it take place below 1065°C. (1950°F.) regardless of the copper content (up to 2 per cent copper). The temperature at which surface cracking appears is independent of the carbon content, but the depth of cracking increases with the carbon content.

46. Theories of Red-shortness.—Just what structural changes effected by the introduction of copper into iron or steel might be responsible for red-shortness has been a subject of controversy among various investigators. The literature on the subject reveals three principal views regarding the mechanism:

a. Red-shortness is caused by oxides.
b. Red-shortness is caused by sulphides of copper or complex sulphides of copper, iron, and manganese.
c. Red-shortness is caused by intergranular films of copper or copper-rich constituent.

Some of the theories are briefly considered below.

a. The Oxide Theories.—Several authors [37,60] advanced the idea that red-shortness is due to oxides of copper which envelop the grains of the alloy and thereby cause intergranular weakness. This opinion, however, is not shared by other investigators. Sargent[60] pointed out that, if the amount of oxygen is so great as to form a dissolved oxide, iron will be oxidized first, and any deoxidizing reagent will reduce the copper oxide first, not the iron oxide. Oxygen by itself has been reported[139] to be without effect on red-shortness of pure iron, provided the sulphur is low (below 0.01 per cent).

This evidence seems to be sufficient to indicate conclusively that red-shortness in copper steels or iron cannot be due to the formation of oxides of copper.

b. The Sulphide Theories.—As in the case of carbon steels, sulphur is also considered by many writers to be directly responsible for red-shortness in copper steels through the formation of intergranular sulphides of copper or complex sulphides of copper, manganese, and iron. The affinity of copper for sulphur is known to be greater than that of iron; therefore, the formation of sulphides of copper is considered possible.

Several investigators claimed that in the presence of sulphur copper forms intergranular films of cuprous sulphide (Cu_2S).[15,28,40,48,153] It has also been observed[133,225,226] that in copper steel the copper and sulphur segregated together to a slight degree, and it was inferred from this that copper may be present in the form of a sulphide. Were such sulphide films formed at the grain boundaries, owing to their low melting point, they would weaken the intergranular cohesion sufficiently to produce red-shortness.

No positive evidence for or against the formation of sulphides of copper is found in the literature. Since other elements are present in steels, the possibility of the existence of pure copper sulphide is doubtful. It is more likely that complex sulphides of iron and copper, or iron, copper, and manganese, would be formed.

Porter[62] suggested that sulphur probably forms a binary eutectic of FeS and Cu_2S (or a ternary eutectic Fe-Cu-S) having a melting point of 870°C. (1600°F.) or about 100°C. (180°F.) below the melting point of the Fe-FeS eutectic.

It was found[173] that a double sulphide of iron and copper [$(Cu_2S)_2FeS$] on cooling disintegrated into $(Cu_2S)_3Fe_2S_3$ and metallic copper at 550°C. (1020°F.). Guertler and Meissner[116] found that on cooling mixtures consisting of 60 per cent copper, 15 per cent sulphur, and 25 per cent iron Cu_2S freezes out at 1077°C. (1970°F.), and free copper (due to sulphur losses) appears at 1025°C. (1875°F.).

Many investigators mentioned that some injurious effects attributed to copper are caused by sulphur. Some consider that in the presence of copper in steel evolution analyses for sulphur are low; *i.e.*, the actual amount of sulphur is higher than is reported[62,175]; but J. T. MacKenzie, in reviewing a draft of this monograph, stated that this is not true.

c. The Copper-film Theory.—In high-copper steels intergranular films of copper-rich constituent appear to be responsible for red-shortness.[33,47,118] By referring to the iron-copper diagram, it will be observed that alloys containing over 8 per cent copper will partially liquate when heated above 1095°C. (2000°F.). A molten copper-rich constituent will be formed on the grain boundaries and will cause red-shortness if the material is worked at such temperatures. When the copper content does not exceed the solubility limit of copper in gamma iron a similar

condition might occur as a result of copper segregation. It will be noted that the lowest temperature (1065°C. or 1950°F.) at which surface fissuring was observed by Lorig and MacLaren in their forging tests roughly coincides with the temperature at which the copper-rich liquid phase appears on heating iron-copper alloys.

47. Causes of Surface Cracking.—As was mentioned before, even in steels with as low as 0.20 per cent copper minute surface cracks are observed in rolling and forging. It has been noted[33,40,206,208] that when a copper steel is heated in an oxidizing atmosphere a coating of copper appears on the surface of the steel underneath the oxide scale. This surface layer of copper was found to be the cause of surface cracking. Stead and Wigham[40] coated a steel wire with a thin layer of copper by applying copper sulphate solutions in several places and heated the wire in a furnace. In the subsequent cold-drawing operation the wire cracked in places where the copper was applied. From this they concluded that the copper alloyed with the surface of the wire, forming a hard brittle skin, and that this skin caused the surface cracking.

Later investigations showed that the surface cracking in hot working is due to penetration of copper into grain boundaries of the steel. Kodama[206] observed that carbon steels containing more than 0.3 per cent copper are subject to surface fissuring on rolling at 1100°C. (2010°F.). Microscopic examination of the fissures in mild steel revealed the presence of a substance colored like copper. Kotaira[208] heated specimens of copper steel at 1000°C. (1830°F.) for 22 hr. and analyzed the surface oxide and the steel below for copper. The analysis showed that only 10 to 20 per cent of the original copper was contained in the oxide skin and that the copper content in the unoxidized steel increased by 5 to 10 per cent. Kodama[206], from similar experiments, concluded that in the surface oxidation of copper steel the copper remains unoxidized and just below the oxide coating, thus increasing the copper concentration of the surface layer of steel.

The conclusions of Kotaira and Kodama were confirmed by Lorig and MacLaren, who made an extensive study of the mechanism of surface fissuring by means of forging tests already described. Figures 38 and 39 illustrate the structure near the surface of a 1.13 per cent copper-steel specimen which was heated for 1 hr. at 1205°C. (2200°F.) and then slowly cooled

to 1065°C. (1950°F.) before being removed from the furnace. Figure 38 is a good illustration of fine threadlike areas of the

FIG. 38.—Outer edge of etched section of a 1.13 per cent copper steel. 170×. (*Lorig and MacLaren.*)

FIG. 39.—Same as Fig. 38. Another area. 170×. (*Lorig and MacLaren.*)

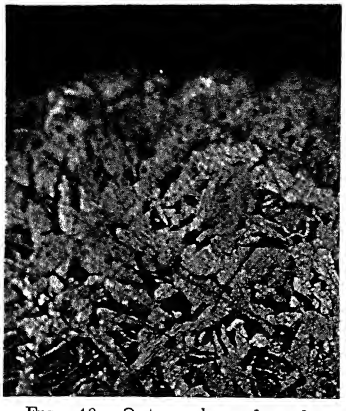


FIG. 40.—Outer edge of carbon steel. Heated 1 hr. at 1205°C. (2200°F.), furnace cooled to 1035°C. (1900°F.). 170×. (*Lorig and MacLaren.*)

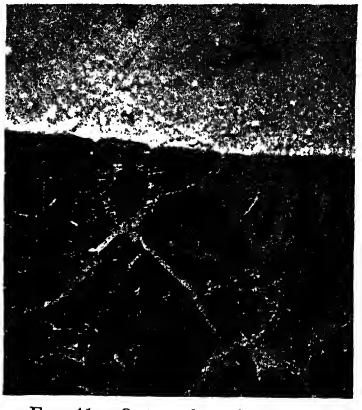


FIG. 41.—Outer edge of etched section of carbon steel sprayed with copper. Heated 1 hr. at 1205°C. (2200°F.), furnace cooled to 1035°C. (1900°F.). 170×. (*Lorig and MacLaren.*)

copper-rich phase interpenetrating the grain boundaries and some copper-rich phase on the surface. Figure 39 shows some darkening at the grain boundaries of the outer crystals of the same

steel. Apparently in this case the copper had been absorbed but had not distributed itself uniformly throughout the crystals. The investigators consider the presence of a decarburized zone somewhat back from the edge as an additional evidence of the enrichment of the surface layer in copper. The pearlitic rim which appears in the copper steel is absent from the decarburized zone of a carbon steel treated identically (Fig. 40).

Specimens of carbon steel sprayed with a thin copper film and forged at 1040°C. (1900°F.) were free from surface fissures (Fig. 41). At 1095°C. (2000°F.), however, the specimens showed the characteristic and somewhat intensified roughening of copper-bearing steels tested at the same temperature. To obtain further evidence, Lorig and MacLaren heated a set of specimens at 1205°C. (2200°F.) for 1 hr. in the presence of nitrogen and charcoal. An examination of the specimens showed that roughening was almost completely eliminated even in those steels which were known to roughen badly when forged after heating in a normal furnace atmosphere for the same time at the same temperature.

These results are sufficiently conclusive to permit the following formulation of the mechanism of surface roughening of copper steels: In heating for rolling or forging, the iron on the surface is oxidized in preference to copper, leaving the copper or the copper-rich iron-copper solid solution on the surface of the steel below the oxide skin. When the temperature employed is above the melting point of this new phase it penetrates into the grain boundaries when the metal is strained and diffuses into the grains. This weakens the cohesion between the surface grains. Any distortion of the grains by rolling, forging, or bending causes the grains to separate, and surface fissuring ensues.

Experimental work of Genders[180] proved that either molten brass or copper penetrated the grain boundaries of mild steel and rendered the material brittle at high temperatures. Schottky, Schichtel, and Stolle[302] showed that copper in contact with steel at temperatures above 1095°C. (2000°F.) produced an embrittlement made evident by cracking of the material subjected to a bend test. Zaharova[339] found that when "pure" iron was held in molten copper no diffusion of copper into the iron occurred but that with commercial iron intergranular diffusion of copper into the iron took place.

48. Prevention of Surface Cracking.—The methods described above do not eliminate surface roughening at temperatures above about 1095°C. (2000°F.). Since it has been definitely established that the surface cracking is due to the accumulation of copper on the surface of the steel because of selective oxidation, and the subsequent penetration into the grain boundaries at temperatures above the melting point of copper, means of preventing the injurious phenomenon suggested themselves. In general, the problem consisted in eliminating the copper film. This could be done in two ways: (1) destroying the film while heating the steels, and (2) preventing its formation or rendering it harmless.

In order to determine whether a highly oxidizing furnace atmosphere would destroy the copper film during its formation, Lorig and MacLaren heated specimens of copper steel at 1205, 1260, and 1315°C. (2200, 2300, and 2400°F.) in a furnace through which a stream of hot air was constantly passing. The highly oxidizing conditions failed to oxidize the copper which was found deposited under the scale.

An attempt to convert copper into a volatile fluoride by heating in a molten sodium-aluminum fluoride salt also failed.

To determine whether or not alloying small amounts of other elements will prevent the deposition of copper under the scale and its penetration into the steel, Lorig and MacLaren made forging tests of a variety of steels. The amount of special elements varied within the following limits:

Element	Percentage
Copper	0.5 to 4.0
Silicon	0.1 to 0.5
Manganese	0.4 to 1.9
Sulphur	0.035 to 0.16
Phosphorus	0.030 to 0.13
Aluminum	0.50 to 1.10
Molybdenum	0.35 to 1.0
Vanadium	0.05 to 0.23
Tin	0.25
Titanium	1.0
Tungsten	1.0
Chromium	0.7 to 1.13
Cobalt	0.22 to 3.50
Nickel	0.30 to 3.50

From the results of the tests Lorig and MacLaren drew the following conclusions:

Manganese does not affect the surface cracking.

Vanadium, zirconium, chromium, and tungsten in amounts investigated have no effect on surface roughening.

Aluminum and titanium seem to increase forging difficulties in copper steel at all temperatures below 1260°C. (2300°F.).

Some improvement in surface appearance may result from additions of about 1 per cent molybdenum.

None of the foregoing elements alters the temperature range where roughening occurs. Tin causes forging difficulties at temperatures below 1040°C. (1900°F.).

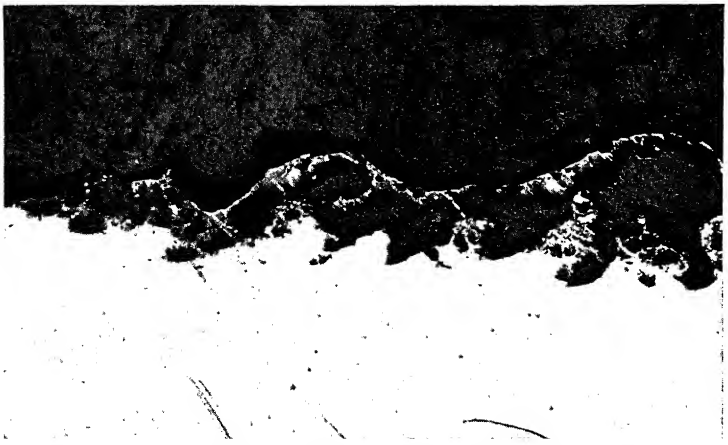


FIG. 42.—Surface cracks in a forged specimen containing 1.07 per cent copper, 0.62 per cent carbon, and 0.31 per cent nickel. Forged at 1205°C. (2200°F.). Unetched. 50×. (*Lorig and MacLaren.*)

High manganese, high silicon with low phosphorus and sulphur contents, high manganese with low sulphur content, and high phosphorus have no effect on the intensity of surface roughening.

Cobalt when present in amounts of about 1 per cent overcomes the roughening.

Nickel has a profound effect in eliminating the roughening of forged copper steels.

The effect of nickel was investigated by means of forging tests at temperatures from 1095 to 1260°C. (2000 to 2300°F.). The copper content of the steels varied from 0.25 to 4.0 per cent. As the result of numerous tests it was found that:

1. Nickel refines the surface checking, but does not eliminate it entirely, and makes the degree of roughening practically independent of the forging temperature and the carbon and copper contents.

2. The amount of nickel required to overcome the surface roughening at given conditions of test is independent of the carbon content.

3. The amount of nickel required for given conditions of test increases with the copper content.

4. The amount of nickel required for a given copper content increases with increased forging or soaking temperature within the range from 1095 to 1175°C. (2000 to 2150°F.) for low-copper steels and at all temperatures for higher copper steels.

It was found further that in low-copper steels forged at 1175°C. (2150°F.) and above less nickel is required than at lower tempera-

FIG. 43.—Surface cracks in a forged specimen containing 1.07 per cent copper, 0.62 per cent carbon, and 1.32 per cent nickel. Forged at 1205°C. (2200°F.). Unetched. 50×. (*Lorig and MacLaren.*)

tures to offset the cracking tendencies of the steel. This was attributed to the action of the scale, which at higher temperatures becomes plastic and glazes the surface.

The effect of nickel content and of forging temperatures on the depth of penetration of cracks is shown in Table 15 and in Figs. 42 and 43.

An illustration of the effect of nickel and of forging temperatures on the surface appearance of forged specimens is given in Fig. 44.

Based on the results of their tests, Lorig and MacLaren suggested the following explanation of the beneficial effect of nickel. The copper accumulated with the nickel under the scale alloys to form a copper-nickel solution. The melting point of the copper film is thereby raised, and the film remains in the solid state at higher temperatures than when nickel is absent, thereby preventing the intergranular penetration.

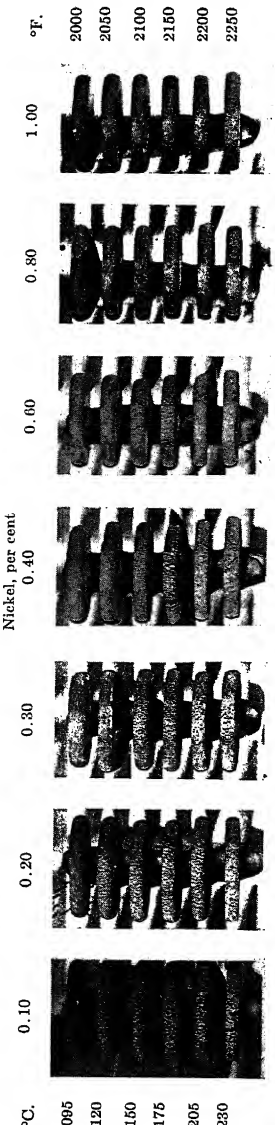


FIG. 44.—Appearance of forged steels containing 0.60 per cent carbon, 1.7 per cent copper, and various amounts of nickel, forged at the temperatures shown. (*Lorig and MacLaren.*)

TABLE 15.—AVERAGE DEPTH OF PENETRATION OF SURFACE CRACKS*

Forging temperature		Composition, per cent			Average penetration, mm.
°C.	°F.	C	Cu	Ni	
1150	2100	0.60	0.80	0.10	0.313
1150	2100	0.60	0.80	0.20	0.187
1150	2100	0.60	0.80	0.30	0.088
1150	2100	0.60	0.80	0.40	0.081
1150	2100	0.60	1.00	0.10	0.417
1150	2100	0.60	1.00	0.20	0.393
1150	2100	0.60	1.00	0.30	0.290
1150	2100	0.60	1.00	0.40	0.131
1205	2200	0.60	1.00	0.10	0.128
1205	2200	0.60	1.00	0.20	0.129
1205	2200	0.60	1.00	0.30	0.119
1205	2200	0.60	1.00	0.40	0.125
1150	2100	0.60	1.70	0.10	0.439
1150	2100	0.60	1.70	0.20	0.485
1150	2100	0.60	1.70	0.30	0.447
1150	2100	0.60	1.70	0.40	0.527
1205	2200	0.60	1.70	0.10	0.540
1205	2200	0.60	1.70	0.20	0.488
1205	2200	0.60	1.70	0.30	0.193
1205	2200	0.60	1.70	0.40	0.136

*Lorig and MacLaren.

The melting point of copper is raised by the addition of nickel as shown below:

Alloy		Melting point	
Copper, per cent	Nickel, per cent	°C.	°F.
100	0	1080	1980
94	6	1095	2000
89	11	1120	2050
79	21	1150	2100
70	30	1175	2150
61	39	1205	2200
54	46	1230	2250
46	54	1260	2300

A fairly good correlation was found by Lorig and MacLaren between the theoretical quantities of nickel required to prevent surface cracking in steels with varying amounts of copper and the actual quantities, although the actual quantities were found to be invariably higher than the computed values (see Table 16). This may be due to the presence of other elements in the copper-rich film. It is also possible that nickel does not alloy with copper in the same proportion as it is present in the steel.

TABLE 16.—ACTUAL AMOUNTS OF NICKEL REQUIRED TO ELIMINATE SURFACE CRACKING IN COPPER STEELS AT VARIOUS TEMPERATURES*

Composition, per cent		Amount of nickel required to overcome surface roughening				
Carbon	Copper	1095°C. (2000°F.)	1095 to 1175°C. (2000 to 2150°F.)	1150°C. (2100°F.)	1205°C. (2200°F.)	1205 to 1230°C. (2200 to 2250°F.)
0.20	0.6	.....	.....	0.30	<0.10	
0.60	0.6	.....	.....	0.30	<0.10	
0.20	1.0	.....	.....	0.40	0.10	
0.60	1.0	.....	.....	0.40	0.10	
0.20	1.2	.....	.....	0.40	0.10	
0.60	1.2	.....	.. ..	0.40	0.10	
0.20	1.7	.....	.....	>0.40	0.30	
0.60	1.7	.....	.....	>0.40	0.30	
0.60	0.25	>0.20				
0.60	0.5	0.20				
0.20–0.60	0.8	0.30				
0.60	1.0	.....	0.40	.....	.....	0.10
0.60	1.2	.....	0.50	.....	.....	0.30
0.60	1.7	.....	0.50 to 0.60	.....	.....	0.40
0.20	1.7	.....	.....	.....	.....	0.40
0.60	2.5	<1.0	1.0	.....	.....	1.20
0.60	4.0	1.5	>1.50	.....	.....	>2.0

* Lorig and MacLaren.

An experiment made at the National Tube Company may serve as a proof of the beneficial effect of nickel. Ingots weighing 300 lb. were prepared at Battelle Memorial Institute. The composition of the ingots was as follows:

Ingot number	Composition, per cent						
	C	Si	Mn	S	P	Cu	Ni
1	0.39	0.23	0.58	0.031	0.020	0.81	0.33
4	0.41	0.25	0.60	.....	.....	1.13	1.00

The ingots were forged, then hot rolled into tubes with a diameter of 1.9 in. and a wall of 0.2 in. Sections of these tubes were further processed by cold drawing into tubes with a diameter of 0.938 in. and a wall of 0.179 in. Surfaces of the tubes were entirely free from checking and other defects traceable to the copper.

It has been found[148] that molten bronze penetrates nickel-bearing steel more easily than plain carbon steel, the reason suggested being the greater solubility of copper in nickel than in iron. It would appear then that a surface film of copper would at high forging temperature penetrate more easily into the steel to which nickel was added, which is seemingly in contradiction to Lorig and MacLaren's findings. This apparent contradiction, however, is easily understood when one considers that nickel also enters in solution with the surface copper layer and raises its melting point to a sufficient degree to keep it solid and thereby prevents its penetration into the steel.

That cobalt appears to have somewhat the same effect as nickel seems at first sight difficult to reconcile with the theory that it is the raising of the melting point of copper by alloying that produces the improvement; for the copper-cobalt alloys do not show a solidus above the melting point of copper. Lorig* pointed out, however, that the range between the liquidus and solidus in these alloys is large and the liquidus is at a high temperature. For example, an alloy of 80 per cent copper, 20 per cent cobalt, starts to freeze at about 1300°C. (2370°F.), and thus some part of the copper is kept solid at all temperatures below this. The removal of some of the copper from the liquid state at the forging temperature is equivalent to having a lower copper content in the steel. The fact that larger amounts of cobalt are required than of nickel is consistent with this explanation.

* Personal communication.

Nehl[366,367] and Rädeker[369] subsequently confirmed the findings of Kotaira and Kodama that surface cracking of copper steel results from the formation of a layer of metallic copper and those of Lorig and MacLaren that the tendency toward surface cracking can be greatly decreased by the addition of nickel. Nehl found that one-half as much nickel as copper is required in order to prevent surface cracking effectively. The commercial production of tubing from copper-nickel steels, as well as the laboratory study, indicated that nickel was effective in preventing surface cracking. Nehl also attributed the good effects of nickel to its raising the melting point of the metallic layer found under the oxide scale. In disagreement with Lorig and MacLaren, he found that the carbon content of the steel had little influence on surface cracking.

It now appears to be definitely established that steels containing less than 2 or possibly 4 per cent copper are not red-short. Steels containing even as little as 0.2 per cent copper, however, when hot worked by the usual practice usually show surface cracks. The severity of the cracking will depend on the conditions under which the steel was heated and the shape of the section fabricated. Several ways of preventing surface cracking may be possible. One, but an unpractical method, is to heat to the working temperature in a reducing atmosphere. Another, which may be just as impracticable, is to hot work the material only at a temperature below 1095°C. (2000°F.). A third method, developed independently here and in Germany, is to add a small amount of nickel to the steel, say one-half as much nickel as copper. The addition of nickel is naturally expensive, but as Nehl pointed out it serves to improve the mechanical properties of the steel as well as to prevent surface cracking.

E. WELDABILITY OF COPPER STEELS

The effect of copper on weldability of iron in the process of puddling was discussed earlier in the chapter. It was brought out that various observations were in fair agreement regarding the amount of copper which can be present in iron without impairing the welding properties of the iron. This permissible maximum was put at about 1 per cent.

This discussion will be primarily concerned with welding copper steel with or without the application of welding rods, and with the effect of copper content of the welding rod on the mechanical

properties of the weld. The literature on the subject indicates that the limiting amount of copper and its general effect are strikingly similar in welding in the puddling process, in hammer welding without any welding metal, and in welding with the application of welding rod.

It must be remembered that observations up to about 1910 refer mainly to pressure welding and to welding up of seams and cracks in forging or rolling.

49. Weldability of High-purity Alloys.—According to Burgess and Aston,[53,57] alloys with copper content below 5 per cent welded easily in forging, and some bars with 7 per cent copper were welded during forging. Alloys containing up to 7 per cent copper could be welded in an electric welder; with higher copper they could not be welded.

50. Some Observations on Welding Copper Steels.—Lipin[33] observed that welding soft steel became difficult when the copper content reached about 0.80 per cent. With 2 per cent copper the welding became impossible. Wrought iron containing 0.65 per cent copper welded perfectly. Clevenger and Ray[70] found that with up to 0.85 per cent copper steel welded well under a drop hammer; with 1.9 per cent copper it welded with difficulty; and with 3 per cent it could not be welded at any temperature. They quoted various authorities to show that it is somewhat more difficult to weld copper steel than it is to weld carbon steel but when the copper is less than 1.0 per cent the weld is stronger than similar steel containing no copper.

Hahn[154] made some welding tests by putting two clean pieces of steel together, heating in air by means of an electric current, and pressing together. Open-hearth steel was used in the tests, the copper varying from 0.58 to 1.92 per cent. The results indicated that the maximum copper content which can be introduced without impairing the welding properties of the steel should not exceed 0.90 per cent. Steels containing above 0.90 per cent copper could not be welded. It was also found that steels containing copper required heating to higher temperatures than copper-free steels. The welded copper steels withstood hot bending well. In cold-bending tests they failed when the copper content exceeded 0.9 per cent. The strength was found to be unaltered.

From these and some other observations[31,38,58,309] the maximum amount of copper permissible without introducing any difficulties in welding appears to be 0.80 to 1.00 per cent.

51. Effect of Copper on Mechanical Properties of Welds.—To investigate the effect of copper on the welding properties of steel, Zeyen and Mehl[309] prepared a series of specimens welded perpendicularly to the direction of rolling by means of electric

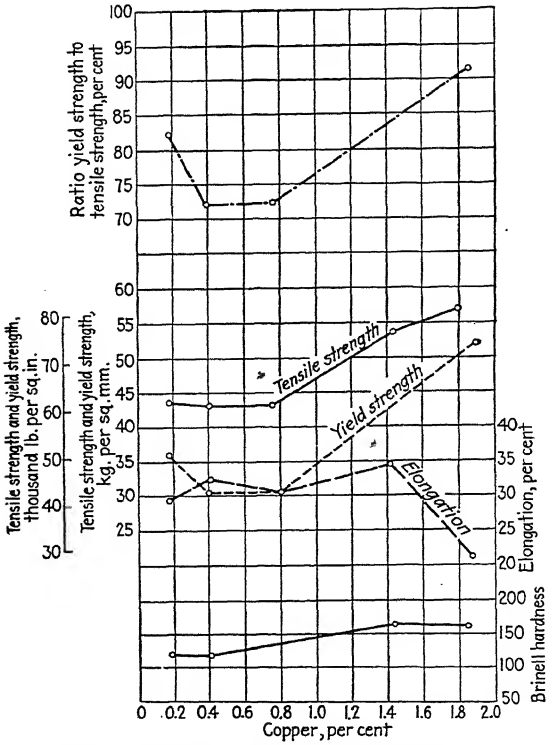


FIG. 45.—Mechanical properties of copper steels in relation to copper content. (*Zeyen and Mehl.*[309])

resistance, electric arc, and an oxy-acetylene torch. The compositions of the steels studied are given below.

Composition, per cent					
C	Si	Mn	P	S	Cu
0.10	0.04	0.58	Below 0.01	Below 0.02	0.17
0.09	0.07	0.35	Below 0.01	Below 0.02	0.37
0.09	0.02	0.52	Below 0.01	Below 0.02	0.75
0.10	0.06	0.68	Below 0.01	Below 0.02	1.47
0.10	0.06	0.60	Below 0.01	Below 0.02	1.96

The strength of welds was determined by tensile and bend tests. The mechanical properties of the parent metal are shown in Fig. 45. The welding rod was of mild carbon steel. The specimens were allowed to cool in air.

As may be seen from comparing Figs. 45 and 46 the electric-resistance welds were satisfactory. The tensile strength

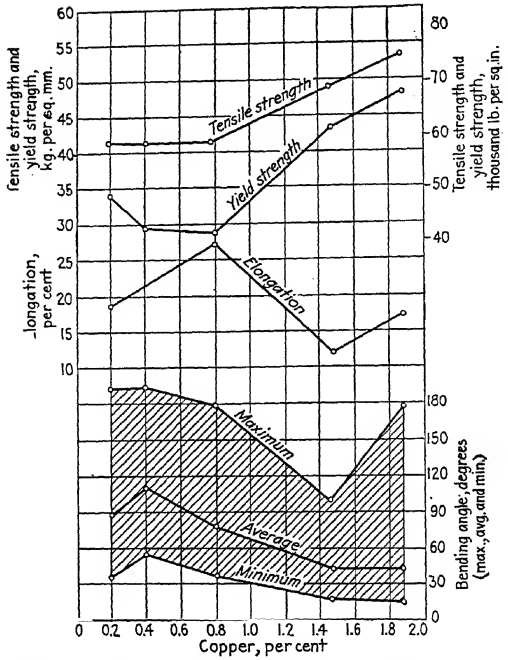


FIG. 46.—Effect of copper on the strength of electric-resistance welds. (*Zeyen and Mehl.*[309])

decreased only to 93 per cent of the original, and the elongation varied between 40 and 90 per cent of the parent metal. Ability to stand bending without cracking was found to be greatest in steels with 0.40 per cent copper; above this copper content it decreased somewhat.

The tensile strength of the arc-welded specimens exceeded that of the unwelded specimens with up to 0.75 per cent copper (Fig. 47). It decreased gradually to about 83 per cent of the

original strength when the copper content reached 2 per cent. Bending tests showed a maximum value at 0.40 per cent copper.

Specimens prepared by the oxy-acetylene torch showed progressive weakening of welds with increasing copper content (Fig. 48). However, up to 0.75 per cent copper the welds were still considered satisfactory, the tensile strength not falling below 90 per cent of the strength of the parent metal. Higher copper

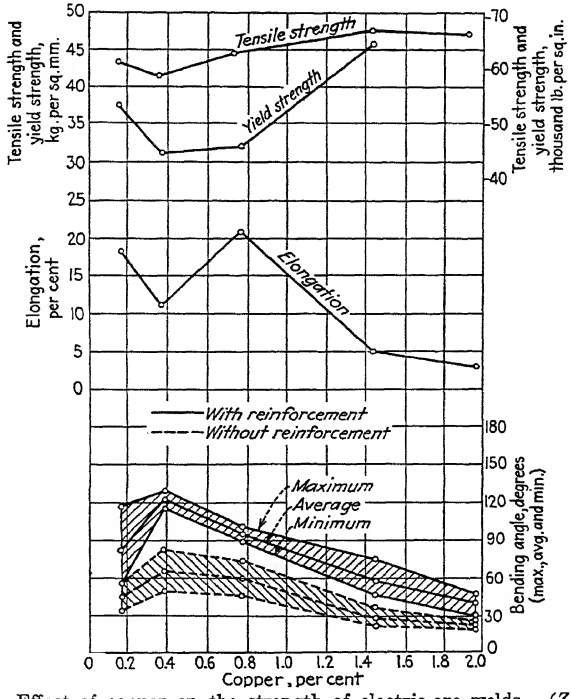


FIG. 47.—Effect of copper on the strength of electric-arc welds. (*Zeyen and*

content weakened the welds considerably. Films of copper or copper oxide were observed on the fractures which occurred just outside of the welded seam.

From the results obtained by Zeyen and Mehl it may be concluded that copper steels containing up to at least 0.75 per cent of copper can be successfully welded by either electric-resistance, electric-arc, or oxy-acetylene method without any appreciable injury to the mechanical properties of the material (Fig. 49).

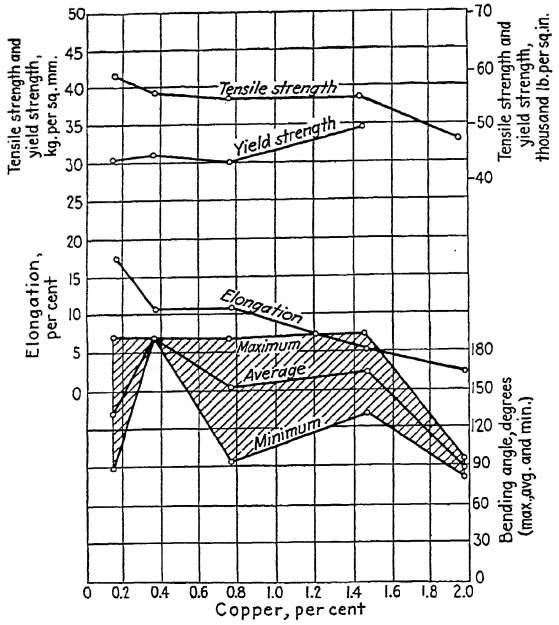


FIG. 48.—Effect of copper on the strength of oxy-acetylene welds. (*Zeyen and Mehl.*[309])

TABLE 17.—MECHANICAL PROPERTIES OF WELDS*

Specimen	Composition of welding bar†		Tensile strength, lb. per sq. in.‡			Elongation in 8 in., per cent‡		
	Mn	Cu	As welded	Precipitation hardened	Normalized and precipitation hardened	As welded	Precipitation hardened	Normalized and precipitation hardened
Parent metal.			60,070			26.7		
Rod 1.....	0.06	0.15	0.0 43,280	39,490	36,450	3.2	1.8	2.5
Rod 2.....	0.06	0.15	1.2 52,880	53,000	53,880	6.6	8.9	10.5
Rod 3.....	0.20	0.40	0.0 47,950	46,140	46,530	4.9	5.9	5.7
Rod 4.....	0.20	0.40	1.2 59,150	56,230	53,400	12.2	13.5	12.4
Rod 5.....	0.20	0.35	0.45 0.0	55,580	47,700	51,880	9.5	5.8
Rod 6.....	0.20	0.35	0.45 1.2	60,430	57,470	56,180	19.6	21.5

* Lorig and MacLaren.
† Phosphorus and sulphur in all rods 0.02 per cent.
‡ Average of two tests.

A summary on the weldability of copper steels based on a questionnaire submitted to metallurgists, fabricators of welded materials, and large consumers, published in *Schmelzschweissung*,[309] confirms the cited conclusions. Leading steel works in Europe and America habitually manufacture welded products from steels containing as much as 0.50 per cent of copper.

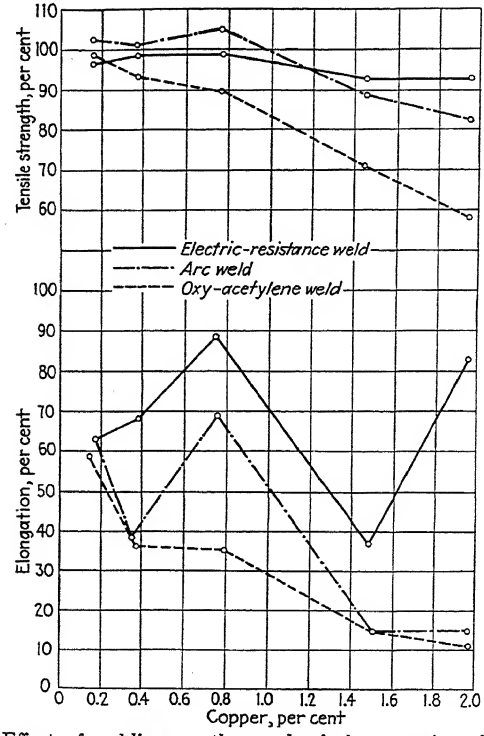


FIG. 49.—Effect of welding on the mechanical properties of copper steel expressed in percentage of the properties of the same material unwelded. (*Zeyen and Mehl.*[309])

The mechanical properties of gas welds made from rods containing 1.2 per cent copper were investigated by Lorig and MacLaren. A series of tensile bars of the double V-notch type were made with copper-free and copper-bearing rods and tested in the as-welded condition, after precipitation hardening, and after normalizing followed by precipitation hardening. Some of the results of the tests given in Table 17 are sufficient to show

that welds made from rods containing 1.2 per cent copper are consistently stronger than welds prepared from unalloyed metal.

In the as-welded bars the strength of the welds made from low-carbon steel was improved to the extent of 22 per cent by the addition of 1.2 per cent copper. The corresponding improvement in the strength of welds made from medium carbon and medium carbon-silicon rods was 23 and 8.5 per cent respectively.

F. EFFECT OF COPPER ON COLD-WORKING PROPERTIES OF STEEL

Very little information is found in the literature on the effect of copper on cold-working properties of steel. It appears from the observations presented below that copper steels containing small amounts of copper, up to about 0.25 per cent, can be cold drawn, rolled, and stamped. No difficulties in the ordinary fabricating processes were reported as being due directly to copper.

Campbell,[26] basing his conclusions on the observation of large amounts of steel, stated that the cold-working properties of steels are not affected by the addition of as much as 1 per cent of copper. Colby[31] reported rolling 4-in. billets of mild steel containing 0.30 per cent copper, and drawing the rods to wire 0.04 in. in diameter without any difficulty. Stead and Wigham[40] as a result of their investigation of adaptability of copper steels containing up to 0.45 per cent copper to wire drawing came to the conclusion that copper in high-carbon steels for wire drawing should be avoided. A later investigation by Wigham[49] indicated that good-quality wire can be obtained from high-carbon steels (0.70 per cent carbon) containing up to 0.25 per cent copper.

According to Genzmer,[37] mild steel to be used for stamping should not contain more than 0.25 per cent copper. Herwig[183] reported that copper renders sheet steel less amenable to dishing out under the press because of strongly adhering scale. Difficulty of removing the scale is said to cause roughness and undesirable appearance of the steel.

Some manufacturers contend that such low amounts of copper as 0.10 per cent are detrimental to deep-drawing properties of sheet. Cupping tests made by Lorig and MacLaren indicated the stiffening of steel with copper. The whole question of the effect of copper upon stamping and deep-drawing properties seems to be primarily one of diverse opinions based on observa-

tions likely to be affected by many variables rather than upon definitely proved facts.

It has been claimed[251] that the addition of small amounts of copper (0.20 to 0.30 per cent) is beneficial in preventing sticking of sheets during rolling.

G. EFFECT OF COPPER ON PICKLING ACTION

No special investigation has come to the authors' knowledge regarding the effect of copper in steel on the action of acids in the pickling operation for removing the scale.

When copper, contained in copper steel or iron, is dissolved together with the iron, it may have an indirect retarding or accelerating effect on the dissolving power of the pickling solution. There is no conclusive evidence, however, to substantiate this statement. It has been suggested[125] that copper in sulphuric acid used for pickling increases the pickling action. Bardenheuer and Thanheiser[312] found that copper in the pickling solution (0.2N H_2SO_4) increases the reaction of steels which on account of the copper content have a low solution rate. This was thought to be due to the electrolytic action between the iron and the deposited copper film.

Other investigators failed to observe any changes in the dissolving action of hydrochloric or sulphuric acids when copper is added to the pickling solution.[119] It seems, however, that copper, when added to nitric acid pickling solution, retards considerably its action on rolled iron but accelerates the action on cast iron.[119] While no conclusive evidence is in existence, it seems reasonable to assume that if copper exerts any effect on the pickling action in one or the other direction the effect is insignificant because of the low concentrations of copper in the solution.

More important is the action of acids on the rust or scale of the materials to be pickled. It has been stated that the scale on steels heated at 1000°C. (1830°F.) retains about 20 per cent of the original copper,[208] but no data have been found in the literature on the influence of the copper content of the scale, or of the pickling solution, on the solubility of the scale. It is well known, however, that the scale on copper steels is more tenacious and more firmly adherent than on plain carbon steels. If it is assumed that there is no great difference in the solubility of mill scale of copper and non-copper steels, it would seem that the tenacity and continuity of the copper-steel scale would con-

tribute to its resistance to the pickling action, first, because of lesser electrolytic effect due to the better continuity of the copper-steel scale, and, second, because the closely adherent scale would shut off the free access of acid to the scale-metal contact surface and thus prevent the spalling effect of the pickling solution. From this point of view, therefore, the action of copper is negative; *i.e.*, copper exerts a retarding action in the pickling operation. Moreover, firmly adhering patches of scale, if unremoved by the pickling solution, may cause considerable trouble in the galvanizing process. The copper film, often observed on pickled copper steels which had been hot worked or heat treated, will not cause any trouble in galvanizing, because the film is very adherent, and the zinc adheres to the film.

Schumacher[376] found that in pickling copper-bearing sheet steel for long periods in either sulphuric or hydrochloric acid a dark film was formed on the surface and that copper was concentrated in this film. Analyses of the steel and the films were:

Element, per cent	Steel	Film from H_2SO_4	Film from HCl
Carbon....	0.035	4.70	5.0
Silicon.....	0.0		
Manganese	0.32	0.27	0.28
Phosphorus	0.026	0.88	1.44
Sulphur....	0.012	1.08	0.18
Copper.....	0.18	20.40	20.16
Nickel.....	0.08	2.36	7.23
Arsenic....	0.043	3.81	6.73

It would seem that, in general, the effect of copper on the pickling of steel is relatively insignificant and at any rate does not interfere with successful galvanizing. This may be inferred from the fact that hundreds of thousands of tons of 0.15 to 0.20 per cent copper steel have been made for structural work, and no trouble has been experienced in hot-dip galvanizing.

Herwig[183] observed that when freshly rolled sheets of copper steel are run into hot water the surface becomes rough and badly spotted, whereas in steels comparatively free from copper the scale flies off leaving gray, smooth surfaces. This spotting and roughening was attributed to the formation of oxide layers which, owing to their copper content, adhere to the metal surface. He

concluded that in rolling steels to sheet for tin plate such spots may easily develop into starting points for cracks or may produce strains and brittleness.

H. AUTHORS' SUMMARY

1. Iron ores often contain small amounts of copper. The copper content of pig iron usually varies from a trace to about 0.20 per cent; occasionally as much as 1 per cent is present.

2. Smelting of cupriferous iron ores does not present any difficulties or peculiarities. All the copper is reduced and is found in the iron.

3. Copper, if present in pig iron in amounts not exceeding about 1 per cent, does not interfere with the puddling. Higher amounts decrease the weldability and make puddling more difficult.

4. The processes of making copper steel and ingot iron, *i.e.*, smelting, refining, pouring, etc., are essentially the same as for copper-free metals.

5. Copper may be added to molten iron or steel in the form of metal, scrap, copper-steel scrap, or cupriferous ore. The metal additions may be made at any time during the making of a heat, preferably to the furnace.

6. Commercial copper steels with usual manganese and sulphur contents can be forged and rolled without difficulty, if the copper content does not exceed about 2 per cent. If present in greater amount, copper causes forging difficulties, but low-carbon alloys with up to 7 per cent copper have been forged on a small scale. Copper-rich alloys can be forged at fair red-heat when the iron content does not exceed some 20 per cent.

7. Forging difficulties in very high copper steels may be caused by intergranular copper films. In high-sulphur, low-manganese steels intergranular films of complex sulphides might be formed. Forging difficulties from such films should be reduced by the addition of manganese.

8. Cracks appear on the edges or even on the entire surface of steels containing as little as 0.20 per cent copper during forging or rolling at temperatures above about 1095°C. (2000°F.). These are due to intergranular penetration of copper deposited under the scale as a result of preferential oxidation of iron during heating as for forging or rolling.

9. Surface cracking may be practically eliminated by the addition of small amounts of nickel, by rolling below the melting point of the copper-rich solid solution, or by preventing the formation of scale while the steel is being heated to the working temperature.

10. Weldability of steel by arc or gas methods is not impaired by copper in amounts up to 0.75 per cent or possibly more. Small amounts of copper in welding-rod metal increase the strength of the weld. The ductility as compared with that of welds made from non-copper welding rod is also increased.

11. Cold-working properties of steel are not injured by small amounts of copper. Low-copper steels can be cold rolled, stamped, or drawn into wire. The true effect of copper on deep-stamping properties is, however, still in dispute.

CHAPTER V

EFFECT OF COPPER ON CHARACTERISTICS AND PHYSICAL PROPERTIES OF IRON AND STEEL

Microstructure and Macrostructure—Effect of Copper on Critical Points—Physical Properties—Carburizing and Nitriding Properties—Authors' Summary

As may be seen from the equilibrium diagram (Fig. 18, page 33), three types of iron-copper alloys should be distinguished: (1) iron-rich alloys—homogeneous solid solutions of copper in iron, (2) copper-rich alloys—homogeneous solid solutions of iron in copper, and (3) alloys of intermediate compositions—heterogeneous mixtures of two solid solutions. Under conditions of apparent equilibrium at ordinary temperature the saturated iron-rich solid solution contains about 0.4 per cent copper, and the saturated copper-rich solution contains about 0.14 per cent iron. In practice, however, these saturation limits may be exceeded either intentionally by application of a proper heat treatment or unintentionally because the precipitation processes in the solid metal are very slow and the equilibrium conditions are not attained with ordinary rates of cooling. The supersaturated solid solutions tend to attain the state of equilibrium and are subject to precipitation hardening at elevated temperatures.

In this chapter the properties of high-purity iron-copper alloys as well as those of commercial irons and steels will be discussed. The high-purity alloys are mainly of theoretical interest, but the study of the properties of such alloys is of great importance, since it makes it possible to investigate the influence of copper alone.

Alloys of the first group, *i.e.*, low-copper homogeneous solid solutions, are most important technically; the copper-rich solid solutions are of lesser importance, and the heterogeneous alloys of intermediate compositions are either unusable or little investigated. This discussion will, therefore, be confined primarily to the low-copper alloys and will include commercial copper steels and irons.

A. MICROSTRUCTURE AND MACROSTRUCTURE

When an alloy containing considerable proportions of copper is heated to a temperature within the regions of liquid immiscibility (the field labeled "two liquids" in Fig. 18, page 33) and held for some time, copper, containing some iron in solution, sinks to the bottom of the crucible owing to its greater specific gravity. Two distinctly separate layers will, therefore, be obtained, the upper layer being iron saturated with copper and the lower layer copper saturated with iron. The composition of each of the liquids depends only on the temperature, while the relative amounts of the two phases depend on the composition of the alloy. An example of a binary iron-copper melt separated into two layers with a very sharp boundary line is shown in Fig. 4 (page 20). It was mentioned in Chapter II that under certain conditions the sharp separation into two layers is not attained, and the copper-rich constituent may be present in the form of very finely divided suspended particles. In such a case the alloy, although it appears homogeneous, will, nevertheless, consist of two phases in the form of an emulsion.

Our interest lies, however, in the character and distribution of copper or copper-rich constituent in the solid alloys which undergo a treatment approximating that of the manufacture of a commercial alloy. It is of interest to note that the question regarding the form and distribution of copper added to iron and steel received considerable attention from early investigators. Since their observations were made on the fractures of specimens either with the help of a low-power microscope or by the unaided eye, and the carbon content was not definitely known, they are not very reliable and should be regarded as rough observations.

52. Structure of Carbonless Alloys of Iron and Copper.—According to Stead,[39] air-cooled cast alloys containing between traces of and 8 per cent copper when fractured show no trace of copper on the broken faces, and the polished metal when examined under the microscope appears free from any copper-colored constituent. Stead also observed that when heated the alloys containing the most copper are the more rapidly colored, and that on heat tinting the crystal grains are not colored equally; oxidation commences at the external boundaries and travels toward the centers of the grains. Stead attributed this unequal tinting to the copper-concentration gradient resulting in the

grains during the solidification, the outward portions of the grains being considered the richest in copper. If more than about 8 per cent is present, the excess copper separates out as a distinct phase. This is illustrated in Fig. 50 showing the microstructure of an alloy containing 10 per cent copper as developed by heat tinting. The black areas between the grains are the copper-rich constituent. The grains consist of a solid solution of copper in iron, the copper concentration being higher at the exterior

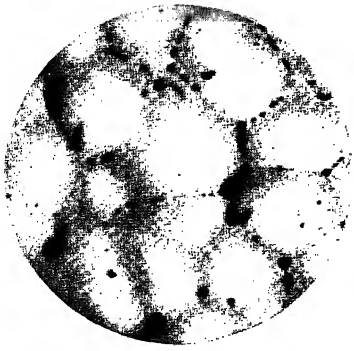


FIG. 50.—Copper 10 per cent, iron 89.6 per cent. Structure developed by heat tinting. White—iron-copper constituent; dark—copper-iron constituent. Showing the graded character of the crystal grains higher in iron at their centers than at the exterior parts. 125 ×. (*Stead.*[39])

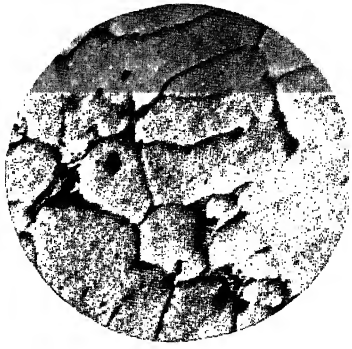


FIG. 51.—Copper 20.5 per cent, iron 79.1 per cent. Structure developed by polishing. White—iron-rich constituent; dark—copper-rich constituent. 125 ×. (*Stead.*[39])

parts than at the centers of the grains. Figure 51 shows the microstructure of an alloy containing 20.5 per cent copper. The copper-rich constituent, the last to solidify, is mainly along the grain boundaries. Typical structures of high-copper heterogeneous alloys are shown in Figs. 52 and 53. The alloys contained 74.5 and 53 per cent copper respectively. In both micrographs the light dendrites are primary iron-rich crystals, and the dark interdendritic ground mass is the copper-rich matrix. It will be noted that as the amount of iron increases these dendrites also increase, gradually crowd together, and assume the form of rounded grains separated by envelopes of copper-rich solution (Figs. 51 and 53). The quantity of this intergranular material is determined by the amount of copper present in the alloy. When copper is low, the iron-rich grains are only partially enveloped by the copper-rich solution.

Another observation of Stead is of interest: that in the alloys of this class the fracture generally follows the copper-rich envelope, and this explains why there is not much difference in the color of the fractured surface of the alloys containing between 90 and 20 per cent copper. In his work on the iron-copper diagram Sahmen[52] observed that the fracture of an alloy containing 85 per cent iron was red, because the fracture is through the crystals of copper-rich solid solution. In the low-copper alloys of this class (about 10 per cent) the network

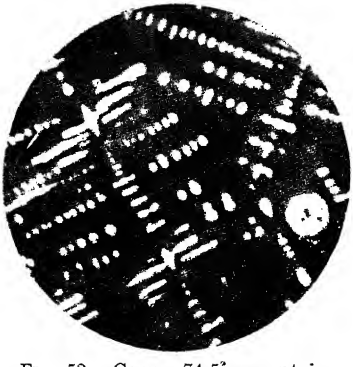


FIG. 52.—Copper 74.5 per cent, iron 25.2 per cent. Structure developed by polishing. White—iron-rich constituent; dark—copper-rich constituent. 125 ×. (*Stead.*[39])

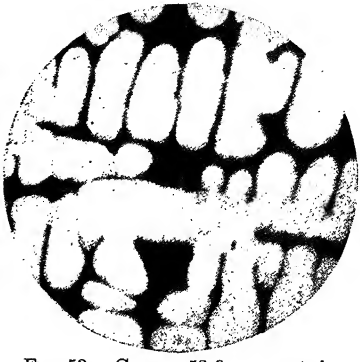


FIG. 53.—Copper 53.0 per cent, iron 46.3 per cent. Structure developed by polishing. White—iron-rich constituent; dark—copper-rich constituent. 125 ×. (*Stead.*[39])

structure of the copper-rich constituent is broken up, and the fracture follows through the copper, then through the iron-rich grains, leaving large areas of copper and iron distributed irregularly over the surface of the fracture and visible without the microscope. The appearance of the sawed or polished surfaces is quite different. As the copper content of the alloy increases, the color gradually changes from that of pure iron to that of pure copper. A low-copper alloy which shows much copper on the fracture has the appearance of iron on the polished surface. Stead pointed out that early observers who judged their alloys only by fractures might have been easily deceived and, therefore, their conclusions must be received with caution.

Pfeiffer[47] claims to have observed the precipitation of minute particles of a copper-rich constituent in an alloy containing 0.5 per cent copper, but this seems improbable.

The microstructure of a cast alloy containing 2.13 per cent copper and 0.15 per cent silicon was examined by Smith.* He observed considerable coring in primary dendrites in small ingots. Higher magnification showed precipitated copper or copper-rich solid solution. In the cast condition alloys with lower copper content showed progressively less precipitation. In the quenched alloy most of the copper is dissolved, and only a few undissolved particles of copper are visible. The alloy quenched from 800°C. (1470°F.) showed considerable undissolved copper. Tempering this alloy at 500°C. (930°F.) produced no visible change in the microstructure.

Attention is called to the fact that Smith's alloy contained 0.15 per cent silicon and some manganese and appeared to be rather dirty.

53. Structure of Copper Steels.—Microstructures of steels containing as much as 4 or 5 per cent copper differ little from copper-free steels containing the same amount of carbon; therefore, it appears to be unnecessary to discuss the structure of copper steels at length.

Microstructures of copper steels having received different treatments were described by Breuil[50] as follows:

SOFT STEELS (0.16 TO 0.18 PER CENT CARBON)

Condition	Copper content, per cent	Microstructure
As cast.....	Low	Pearlite in fine filaments
As cast.....	4	Ferrite more subdivided. Fine filaments of cementite along grain boundaries
As cast.....	8	Ferrite becomes fine
As cast.....	16	Numerous copper-rich filaments
As cast.....	32	These filaments spread throughout the entire mass forming a dendritic network corresponding with the solidification figure of cementite which accompanies it
Annealed.....	Low	Fine ferrite and pearlite
Annealed.....	4 to 8	Reddish coloration, particularly around the edges of pearlite grains
Annealed.....	16	Filaments of copper-rich constituent altered into scattered globules in a fine ferrite-pearlite matrix

* Unpublished report by C. S. Smith of the American Brass Company.

SEMIHARD STEELS (0.28 TO 0.42 PER CENT CARBON)

Condition	Copper content, per cent	Microstructure
Cast	0 to 8	Same as in soft steels
Cast	16	Copper-rich globules
Cast	32	Considerable segregation. Skin of ingots consists of pearlite + copper-rich globules, core copper-rich phase + iron-rich dendrites
Annealed	0 to 8	Free ferrite increased by the dissociation of pearlite of cast steels. Ferrite grains the smaller the higher the copper content. Copper, therefore, hinders the crystallization of iron
Annealed	16 to 32	Copper segregates and tends to melt out of steel

HARD STEELS (0.56 TO 0.80 PER CENT CARBON)

Condition	Copper content, per cent	Microstructure
Cast	10	Scattered globules of copper-rich constituent
Cast	20	Globules more numerous and larger
Cast	30	Liquation occurs
Cast	0 to 30	Structure fine pearlitic
Annealed	0 to 30	Fine-pearlitic structure is maintained on annealing

SOFT STEELS

Condition	Copper content, per cent	Microstructure
As rolled	0 to 4	Structure same as in plain carbon steels in as-rolled, annealed, or quenched conditions; however, pearlite in copper steels is finer and permeates the steel in proportion as the percentage of copper increases
As rolled	7	Pearlite contains threads of cementite and ferrite. In these steels annealing effects considerable change. Martensite is finer than in copper-free steels

SEMIHARD STEELS

As rolled.	Same conclusions as for soft steels

HARD STEELS

Condition	Copper content, per cent	Microstructure
As rolled.....	10	Extremely fine pearlite-sorbite and martensite. Copper-rich globules extremely fine. Quenching does not yield martensite. Reheating causes coalescence of copper-rich globules

A number of investigators[39,50,70,203,219,279,291,325] found that copper tended to refine the structure of steel. Reed,[332] however, claimed that copper increased the grain size of cast steels of medium carbon content.

According to Stogoff and Messkin,[219] from 1 to 5 per cent copper has but little influence on the structure of quenched and tempered steels containing between 0.65 and 1.20 per cent carbon. According to Hayward and Johnston,[88] quenched copper steels contain slightly more martensite than copper-free steels.

It was reported by Ishiwara and associates[166] that steels containing from 1.11 to 1.27 per cent carbon and from 3 to 4.85 per cent copper graphitized rapidly at temperatures above 1100°C. (2010°F.). Reed,[332] however, failed to observe graphitization in high-copper, high-carbon steels subjected to long annealing treatments.

According to Isihara,[156] copper widens the temperature range throughout which annealing produces spheroidized cementite.

B. EFFECT OF COPPER ON THE CRITICAL POINTS OF IRON AND STEEL

As was shown in Chapter II, the effect of copper on the allotropic transformations is similar to that of carbon. They both raise the A_4 point and depress the A_3 point, and both form the same type of gamma field, the effect of one being intensified by the presence of the other. Osmond [20] found that elements of low atomic volume in each period of the periodic system, such as carbon, boron, nickel, manganese, and copper, lower the temperature at which gamma iron is stable. According to his generaliza-

tion, elements of low atomic volume tend to make iron assume or preserve the particular molecular form in which it has itself its lowest atomic volume, the converse being the case with elements

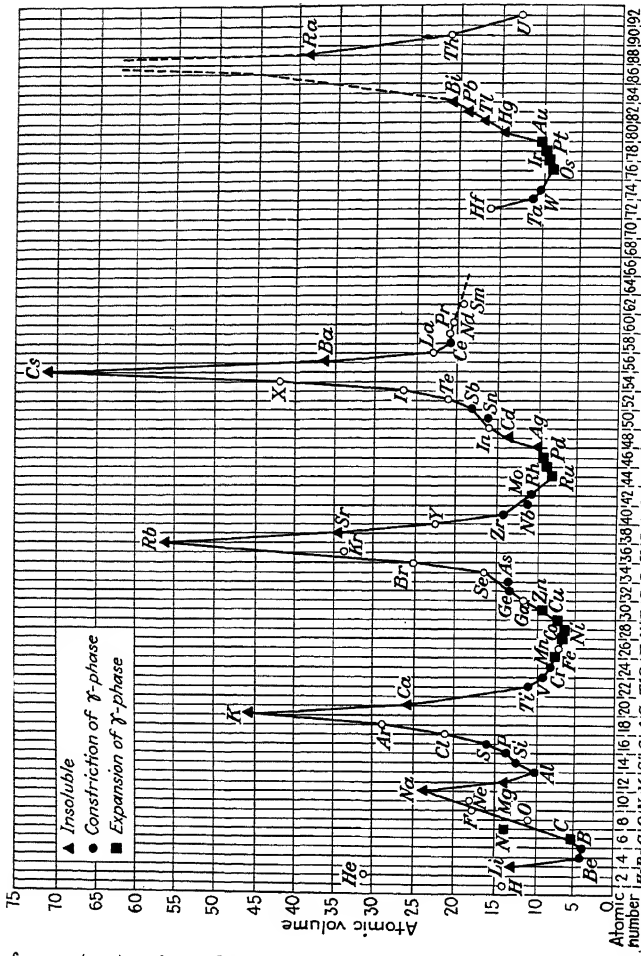


FIG. 54.—Effect of various elements on the type of gamma field of iron alloys. (*Wever.*[253])

of great atomic volume. Figure 54 taken from the work of Wever[253] shows the relation between atomic volumes and the influence of elements on the type of gamma field of iron alloys.

If one had to deal with the binary iron-copper, or ternary iron-copper-carbon alloys of high purity, the critical temperatures

could be read directly from the constitutional diagrams of the corresponding systems. The diagrams represent the state of the alloys at equilibrium, which can be attained only when the system is given sufficient time for the completion of the changes; in practice, however, it is not usually possible to hold the materials at the required temperatures for a long time. It must also be borne in mind that the condition of the metal depends on heating and cooling rates and on the maximum temperatures to which the metal is subjected during the heat-treating operations.

54. Effect of Maximum Heating Temperature on the Critical Points of Iron-copper Alloys.—As was mentioned in Chapter II, in their thermal determination of the gamma-alpha transformation of iron-copper alloys, Ruer and coworkers[73,85] observed that the temperature of the transformation is different according to whether the alloy was cooled directly from the molten state or was reheated to the transformation temperature after solidification and cooling to room temperature. The transformation was also found to take place at higher temperatures when lower maximum temperatures had been found on previous heating.

55. Effect of Rate of Cooling on the Critical Points of Iron-copper Alloys.—Ruer and coworkers observed no effect of cooling rate on the temperature of the gamma-alpha transformation. Buchholtz and Köster,[257] however, found that the gamma-alpha transformation of low-carbon copper steels is influenced by the rate of cooling. They found that, if a steel containing 0.04 per cent carbon, 0.18 per cent silicon, 0.16 per cent manganese, and 5 per cent copper is cooled in the furnace, the transformation takes place at 780°C. (1435°F.); on air cooling it occurs at 725°C. (1335°F.).

56. Critical Points of the Ternary Alloys of Iron, Copper, and Carbon.—According to Ishiwara and coworkers,[166] the eutectoid temperature, 833°C. (1530°F.), of the iron-copper alloys is lowered to about 700°C. (1290°F.) by the addition of 0.9 per cent carbon. The temperature of the pearlitic transformation of the iron-carbon system (A_1) is lowered from 720°C. (1330°F.) to 700°C. (1290°F.) by addition of 1.75 per cent copper.

The effect of carbon on the critical points of iron-copper alloys was studied by means of thermal analysis under conditions approaching equilibrium as nearly as it was practicable to attain. The results were presented in tables in Chapter III, where the thermal arrests are given for series of iron-copper alloys with

carbon content varying in steps of about 0.5 per cent and also in other tables and curves throughout the chapter. This work is the only available source of information on the subject.

From dilatometric analyses Rädeker[369] found that the A_1 temperature was lowered 10°C. (18°F.) for each per cent of copper; only steels containing up to 1.5 per cent copper were studied.

57. Critical Points in Copper Steels.—Critical points of copper steels as determined by different workers are listed in Table 18. These determinations in general indicate that copper lowers the A_3 and A_1 transformations. The differences in actual values are, of course, largely due to differences in compositions and in the rates of cooling. The temperatures are not necessarily equilibrium temperatures but represent points determined by the usual procedure of "slow cooling."

Critical points of high-carbon copper steels were studied by Stogoff and Messkin.[219] It may be seen from Table 19 that the values of Ac_1 determined by differential thermal analysis are lower than those obtained by dilatometric analysis, and the Ar_1 values are higher. This is attributed to the difference in the rate of heating: the samples for thermal analysis were heated to temperatures between 930 and 980°C. in 3.5 hr. and cooled to temperatures of 300 to 350°C. in 4 hr. For dilatometric analysis the time of heating to 1000°C. was 40 min. and of cooling to 250°C. was 1 hr. It will be noted that, on cooling, copper retards the A_1 transformation and produces considerable lag. The values obtained by dilatometric analysis are somewhat lower than those determined by thermal analysis, perhaps because of the slightly higher heating temperatures in dilatometric analysis. The average value of the A_1 point (about 700°C.) agrees closely with the eutectoid temperature for ternary iron-carbon-copper alloys determined by Ishiwara, Yonekura, and Ishigaki (Chapter III).

These results were in general confirmed by the work of Lewis[325] on low-copper steels. He heated his steels in a vacuum and took cooling curves beginning from 960°C. in all cases. The compositions of the steels and the results obtained are given in Table 20.

These values, when compared with those of copper-free steels, showed a slight lowering of the critical points brought about by the copper. This lowering is also apparent when the individual steels of different copper content are compared. In all cases

TABLE 18.—CRITICAL POINTS OF COPPER STEELS OBTAINED BY VARIOUS INVESTIGATORS

Authority	Composition, per cent			Critical temperatures, °C.						Method of determination
	C	Cu	Mn	Ar_3	Ac_3	Ar_2	Ac_2	Ar_1	Ac_1	
Osmond[30]	0.102	0.347	0.28	810	...	710	...	655	.....	Thermal
	0.183	4.10	0.28	.....	...	720	...	615		
	0.10	4.44	0.28	.....	...	720	...	605		
Arnold[24]	0.10	1.81	0.08	.....	815	716	716	654	.....	Thermal
Curie[30]	0.87	3.95	.....	.....	...	658	701			
Clevenger and Ray[70]	0.46	0.0	0.03 to 0.05	.....	...	.....	...	730	.....	Thermal
	0.46	4.5	.....	.....	...	.....	...	635		
Hadfield[288]	1.0	0.0	.....	.....	...	.....	...	730 to 705	755 to 775	Dilatometric
	1.0	2.79	.....	.....	...	.....	...	695 to 665	735 to 755	
Breuil[45,60]	0.168	0.0	.....	870	...	780	...	.....	.....	Thermal
	0.156	1.0	.....	850	...	715				
	0.156	2.0	.....	820	...	730				
	0.165	4.0	.....	780	...	.....	...	670		
	0.103	8.0	.....	730						
	0.336	0.0	.....	950	...	780	...	720		
	0.40	1.0	.....	980	...	725	...	680		
	0.39	2.0	.....	980	...	730	...	680		
	0.37	4.0	.....	980 to 872	...	750	...	678		
	0.31	8.0	.....	975 to 865	...	700	...	645		
	0.41	16.0	.....	975 to 872	...	670 to 700	...	630		
Reed[332]	1.13	4.5	.....	.....	...	.....	...	644	.....	Thermal
	1.13	8.7	.....	.....	...	.....	...	648		
	1.13	?	.....	.....	725					
	1.13	10.0	.....	.....	775					
	1.13	5.0	.....	770						
French[126]	0.06	0.24	.....	882	916	767	773	.....	.....	Thermal
Boylston[195]	*	0.0	.....	880	919	760	774	.....	.....	Thermal
	*	0.25	.....	871	913	762	770			
	*	5.0	.....	798	870	757	765			

* Armco iron.

TABLE 19.—CRITICAL POINTS OF COPPER STEELS*

Composition, per cent				Critical points, °C.							
				Thermal analysis				Dilatometric analysis			
C	Cu	Si	Mn	Ac_1	Ar_1	Hysteresis	Maximum heating temperature	Ac_1	Ar_1	Hysteresis	Maximum heating temperature
0.87	1.19	0.06	0.14	722	675	47	950	720	640	80	1000
0.76	3.03	0.16	0.21	730	678	52	935	735	655	80	1000
0.69	4.81	0.06	0.31	715	665	50	930	730	640	90	1000
1.11	1.42	0.07	0.17	720	685	35	940	740	675	65	1000
1.07	3.25	0.08	0.22	...	...	..	...	740	665	75	1000
1.03	5.07	0.09	0.14	715	660	55	940	740	665	75	1000
0.74	1.41	0.16	0.34	725	665	60	980	735	645	90	1000
1.22	1.27	0.12	0.15	715	690	25	975	...	...	..	1000

* Stogoff and Messkin.[219]

TABLE 20.—CRITICAL POINTS OF COPPER STEELS*

Composition, per cent							Critical temperatures,		
C	Si	S	P	Mn	Cu	Other elements	Ar_3		
0.10	Trace	0.023	0.05	0.41	0.22		855	758	650
0.12	0.01	0.04	0.025	0.42	0.10		860	762	683
0.14	Trace	0.048	0.023	0.49	0.38		827	746	656
0.15	0.052	0 029	0.034	0.56	0.05		850	758	687
0.16	0.047	0.023	0.021	0.58	0.36		830	750	656
0.20	0.056	0.031	0.037	0.64	0.10		830	753	654
0.19	Trace	0 04	0.05	0.70	0.29		824	752	654
0.20	0.07	.026	0.024	0.64	0.75		834	761	650
0.23	0.12	.029	0.026	0.50	0.05		827	753	671
0.60	0.19	036	0.035	0.54	0.05		717†	717†	682
0.60	0.15	031	0.036	0.58	0.36		703†	703†	669
0.33	0.16	032	0.027	0.60	0.52	0.39 Cr	745	723	659
0.03	0.01	035	0.01	0.20	0.45	0.10 Mo	864	755	not noted

* Lewis[325]

† A_{3-2} point.

the A_1 point appears to be lowered much more than the A_2 and A_3 points.

Burgess and Woodward[112] stated that when copper is substituted for part of the nickel in nickel steels the effect of copper is apparently the same as that of equal amounts of nickel. Steel with 0.58 per cent carbon, 2.45 per cent nickel, and 0.62 per cent copper showed critical points which would be expected for a similar nickel steel containing 0.58 per cent carbon and 3 per cent nickel.

C. PHYSICAL PROPERTIES

The physical properties of iron-copper alloys will be considered here in relation to heat treatment, temperature, and mechanical working. Precipitation-hardening phenomena will be omitted here, because a separate chapter is devoted to that subject. Most of the data available in the literature refer to alloys prepared for experimental purposes, and very little information is found on the physical properties of commercial irons and steels. It is apparent, however, that generally there is not much difference between commercial products and pure iron of the same copper content; properties vary only with the methods of manufacture and the amount of impurities present.

58. Electric Properties of High-purity Alloys.—Burgess and Aston[56] prepared a series of alloys with copper varying from 0.09 to 7.05 per cent. A typical alloy contained 0.047 per cent carbon, 0.005 per cent sulphur, 0.062 per cent silicon, and 0.016 per cent phosphorus. The alloys were forged into $\frac{5}{8}$-in. rounds and quenched from 900°C. (1650°F.). For comparison, a standard bar of electrolytic iron and a bar containing 94.34 per cent copper were also used. In Table 21 the resistance data are given in microhms per cubic centimeter and also in terms of relative resistance compared with the standard bar.

In their investigation of the iron-copper alloys Ruer and Fick[73] determined the resistance of a series of alloys representing an entire section across the diagram. Since the alloys containing between 6 and 80 per cent of copper could not be forged, they were cast and turned to the required diameter. All the specimens were heated to 1000°C. (1830°F.) and cooled slowly. It was noticed that no appreciable change in resistance was caused by annealing. Results are given in Table 22.

TABLE 21.—ELECTRIC RESISTANCE OF IRON-COPPER ALLOYS*

Copper, per cent	Microhms per cu. cm.	Relative resistance
0.09	12.2	1.01
0.20	12.0	0.99
0.42	13.6	1.12
0.80	13.6	1.12
1.01	14.7	1.22
1.51	17.0	1.41
2.01	13.4	1.11
3.99	12.7	1.05
5.07	12.5	1.03
6.16	12.7	1.05
7.05	15.8	1.31
94.34	3.9	0.24

* Burgess and Aston.[5]

TABLE 22.—ELECTRIC RESISTANCE AND CONDUCTIVITY OF ANNEALED IRON-COPPER ALLOYS*

Iron, per cent by weight	Resistance, microhms per cu. cm.	Conductivity per cu. cm. in 10^4 mhos	Iron, per cent by weight	Resistance, microhms per cu. cm.	Conductivity per cu. cm. in 10^4 mhos
100	11.84	8.45	50	6.37	15.69
99.5	13.70	7.30	45	6.33	15.80
99.0	16.04	6.23	40	5.77	17.34
98.5	14.00	7.14	35	5.55	18.02
98	14.00	7.14	30	4.99	20.06
97	14.00	7.14	25	4.77	20.97
96	13.01	7.69	20	4.47	22.40
95	12.53	7.98	15	4.08	24.50
94	12.27	8.15	10	3.99	25.07
93	12.27	8.15	8	3.87	25.85
92	11.84	8.45	6	3.75	26.70
91	11.49	8.70	4	3.66	27.36
90	11.36	8.80	3	3.64	27.45
85	10.54	9.49	2	3.60	27.80
80	10.10	9.90	1.5	3.51	28.49
75	9.45	10.58	1	3.36	29.76
70	8.63	11.59	0.8	3.36	29.76
65	7.72	12.96	0.5	3.16	31.65
60	7.28	13.73	0	1.93	51.81
55	7.02	14.24			

* Ruer and Fick.[73]

59. Effect of Copper on the Electric Resistance of Steel.*—Dillner[27] showed that the electric resistance of steels is increased by the addition of copper up to at least 0.62 per cent and that in this respect copper acts as any other element dissolved in iron.

As reported by Breuil,[50] Fric showed that the maximum electric resistance of steel is attained at a copper content which is the lower the higher the carbon content. This may have some relation to the amount of copper dissolved in iron, which is presumably the greater the lower the carbon (Table 23).

Electric-resistance tests showed a well-defined maximum for each series examined, which was determined at

2 per cent copper for steels with 0.15 per cent carbon,
1.7 per cent copper for steels with 0.35 per cent carbon,
0.5 per cent copper for steels with 0.70 to 1.0 per cent carbon.

TABLE 23.—ELECTRIC RESISTANCE OF ROLLED BARS AT 10 TO 12°C. (50 TO 54°F.)*

Copper, per cent	Specific resistance, microhms per cu. cm.			
	Mild steel 0.15 per cent C	Semihard steel 0.35 per cent C	Hard steel 0.7 per cent C	Very hard steel 1.0 per cent C
0.0	13.81	16.95	20.55	22.58
0.5	15.06	17.69	22.03	24.86
1.0	16.69	18.76	21.13	24.72
2.0	17.46	19.01		
3.0	.....	.....	20.90	24.24
4.0	16.71	17.76		
10.0	.....	.....	19.81	

* Breuil.[50]

60. Effect of Copper on Magnetic Properties of Iron-copper Alloys.—One of the earliest references to the influence of copper on the magnetic properties of iron is found in Percy's "Metallurgy."[11] According to Percy, Karsten observed that copper appeared to have very little effect on the magnetic property of iron, as the presence of very small quantities of iron in copper may be detected by a magnet. Percy also noted that alloys prepared in his laboratory, containing from 20 to 85 per cent copper acted strongly on the magnetic needle. In 1891, Howe[22]

* See also page 25 for influence of copper on resistance of low-carbon steels.

made the following statement substantiated by references from the literature. Alloys with 41.75 per cent, 50 per cent, and 80 per cent copper are strongly magnetic; the alloy with 94 per cent copper is magnetic. Sahmen[52] found that pure iron-copper alloys containing 98.7 per cent copper are magnetic at ordinary temperatures; alloys with 99 per cent copper are non-magnetic.

The effect of copper content and of heat treatment on the magnetic properties of iron-copper alloys of high purity was

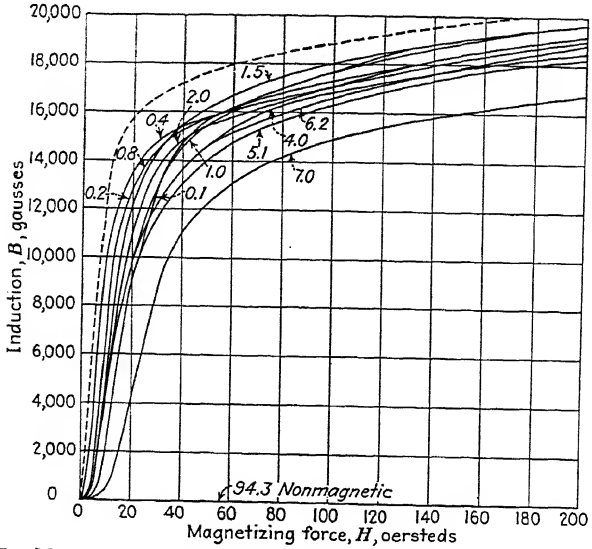


FIG. 55.—Magnetization curves of iron-copper alloys. Unannealed. (*Burgess and Aston.*[56])

investigated by Burgess and Aston.[56] Ingots weighing 1 lb. were prepared from electrolytic iron and electrolytic copper and forged into ⅝-in. rounds. The analysis of one bar was 0.047 per cent carbon, 0.005 per cent sulphur, 0.062 per cent silicon, and 0.016 per cent phosphorus. The magnetic tests were made with an Esterline permeameter using the following samples: (1) as forged, (2) annealed at 675°C. (1245°F.), (3) annealed at 1000°C. (1830°F.), and (4) quenched from 900°C. (1650°F.). All tests were compared with a standard bar of electrolytic iron. As may be seen from Fig. 55,* the permeability of the as-forged alloys

* As there is nothing in the original paper to indicate the contrary, it may be assumed that in Fig. 55 values for alloys with 0.2 and 0.8 per cent copper

fell off rapidly as the copper content exceeded 2 per cent. The alloy with 7 per cent was poor; the alloy with 94.3 per cent of copper was found to be non-magnetic. Annealing at 675°C. (1245°F.) greatly improved the quality of all specimens, and the curves (Fig. 56) show a gradual decrease in permeability with increase in copper content. The alloys with 0.422 and 0.804 per cent copper were found to be the best of the series, the former being but little inferior to the standard electrolytic iron. The

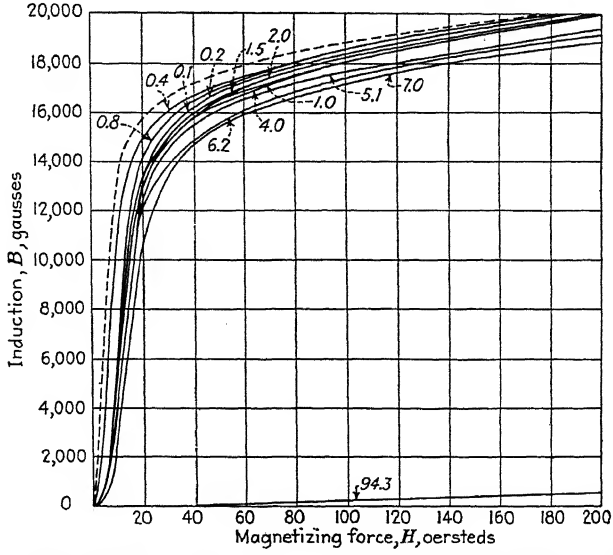


FIG. 56.—Magnetization curves of iron-copper alloys. Annealed at 675°C. (1250°F.). (*Burgess and Aston.*[56])

effect of annealing at 1000°C. (1830°F.) was very slight (Fig. 57). It did not change the relative positions of the curves but decreased the flux densities reached in the upper ranges. For the values of H below 10, the permeability of the alloys with less than 1 per cent copper increased, but the alloys with over 1 per cent showed a decrease for all values of H. Quenching from 900°C. (1650°F.) (Fig. 58) resulted in practically no change in quality from that obtained by annealing at 1000°C. (1830°F.). The bar containing 94.34 per cent copper showed a small magnetic flux in the

fall on the same curve. This is also the case with alloys 0.1 and 0.2 in Fig. 56, with alloys 0.4 and 0.8 in Fig. 57, and with alloys 0.2 and 0.8, also 1.5 and 4.0 in Fig. 58.

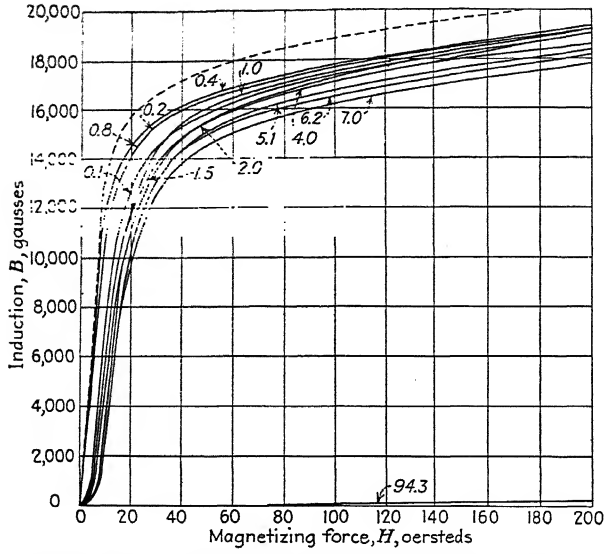


FIG. 57.—Magnetization curves of iron-copper alloys. Annealed at 1000°C. (1830°F.). (*Burgess and Aston.*[56])

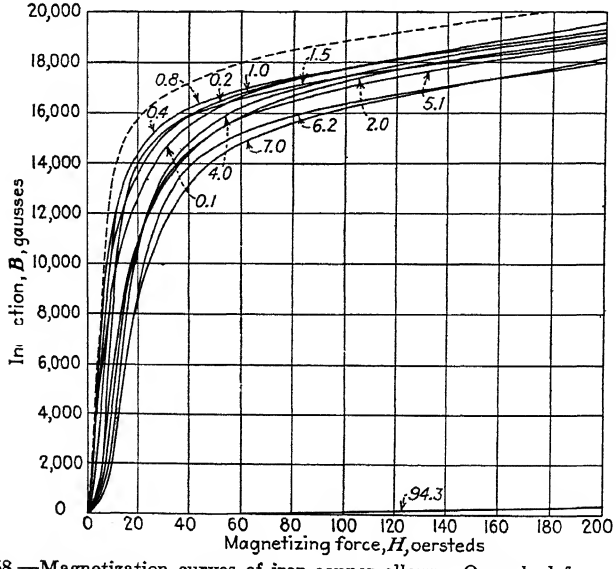


FIG. 58.—Magnetization curves of iron-copper alloys. Quenched from 900°C. (1650°F.). (*Burgess and* .

TABLE 24.—COERCIVE FORCE AND RESIDUAL INDUCTION OF IRON-COPPER ALLOYS*

Copper, per cent	Coercive force, oersteds; H(max.) = 200				Residual induction, gausses; H(max.) = 200			
	Unannealed	Annealed at 675°C. (1245°F.)	Annealed at 1000°C. (1830°F.)	Quenched from 900°C. (1650°F.)	Unannealed	Annealed at 675°C. (1245°F.)	Annealed at 1000°C. (1830°F.)	Quenched from 900°C. (1650°F.)
0.00	5.5	6.2	3.1	2.5	12,300	13,800	10,000	8,000
0.09	13.0	8.7	12.1	4.3	12,700	12,000	10,100	8,400
0.20	7.0	9.3	4.0	3.5	11,100	13,300	8,400	8,400
0.42	7.0	6.0	3.7	3.6	9,900	13,300	8,600	9,300
0.80	9.5	9.5	4.1	4.3	11,500	14,900	8,700	9,100
1.01	14.0	9.5	8.8	5.4	11,100	14,500	10,400	8,700
1.51	12.8	10.5	11.3	7.3	11,100	14,300	12,400	12,500
2.00	10.7	10.0	9.0	8.3	10,200	12,800	10,200	9,900
3.99	6.0	9.8	9.3	9.7	9,200	13,200	11,100	11,300
5.07	5.7	10.9	11.5	11.2	8,300	13,200	11,500	11,700
6.16	12.5	10.5	11.8	11.8	9,300	11,600	11,800	12,100
7.05	12.5	13.2	12.5	12.6	7,700	12,500	13,100	11,200
94.34	Non-magnetic	200+	200+	200+	Non-magnetic	500	300	400

* Burgess and Aston.[56]

annealed and the quenched conditions, but the amount was so slight that the authors classified this material as non-magnetic.

The results of measurements of coercive force and residual induction are presented in Table 24. The investigators did not draw any specific deductions from their residual-induction values. Coercive force, in general, was found to diminish with successive treatments, although in a few cases the reverse was true.

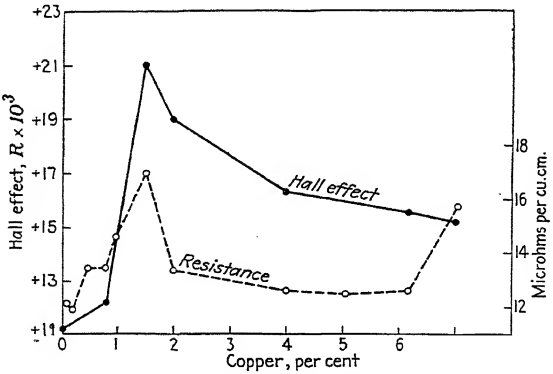


FIG. 59.—Specific resistance and Hall effect of iron-copper alloys. and *Burgess* (

Summarizing their results, Burgess and Aston stated that, in general, the magnetic quality of the alloys deteriorates almost in proportion to the copper content, and, therefore, there is no advantage to be gained by adding copper to iron if a good magnetic permeability is wanted. On the other hand, they thought that there is nothing to be feared from the effect upon the magnetic quality of the small percentage of copper ordinarily found in commercial materials. Since the permeabilities of alloys with small amounts of copper are sufficiently high for commercial purposes, they suggested that 1 to 2 per cent copper be added if an alloy of greater tensile strength is desired.

61. The Hall Effect.—Smith[120] determined the Hall effect using the samples prepared by Burgess and Aston[56] in which the copper content varied from nil to 7 per cent. The maximum Hall effect was obtained on the samples with 1.5 per cent copper. The variation with composition is similar to the variation of electric resistance. This is shown in Fig. 59 where the spe-

cific resistance obtained by Burgess and Aston is plotted for comparison.

62. Effect of Heat Treatment on Magnetic Properties.—To determine the heat treatment which would produce the best magnetic qualities, Ross[63] investigated a series of iron-copper alloys containing 0.01, 0.13, 0.20, 0.39, 1.05, 1.88, 3.37, 5.01, and 6.95 per cent copper. A typical alloy contained 0.05 per cent carbon, 0.07 per cent manganese, and less than 0.01 per cent each of silicon, phosphorus, and sulphur. The tests were made in a Gray-Ross magnetometer on bars in five different conditions: (1) as forged, (2) annealed at dull red, (3) annealed at 600°C. (1110°F.), (4) annealed at 900°C. (1650°F.), and (5) quenched in iced brine from 900°C. (1650°F.). It should be noted that work done prior to understanding of precipitation hardening of iron-copper alloys covers only materials not intentionally precipitation hardened.

Experiments of Ross in general confirmed the results obtained by Burgess and Aston and led him to similar conclusions. He suggested adding small amounts of copper in cases where increased tensile strength is desired. The amount of copper should not exceed about 0.5 per cent unless the resultant loss in magnetic quality is thought to be more than compensated by the gain in tensile strength. The best magnetic qualities are obtained on alloys normalized at dull red heat; annealing at higher temperatures is not recommended, because it tends to diminish permeability and also makes the alloy less strong, especially if some carbon is present.

Kussmann and Scharnow[237,238] investigated the magnetic properties of a series of alloys with varying copper content. Their specimens were prepared by melting together electrolytic iron and copper in an induction furnace under vacuum. The ingots were hammered, drawn to a diameter of 6 mm. (0.24 in.), and annealed in a vacuum for 8 hr. at 800°C. (1470°F.). Magnetic saturation was determined using the yoke-isthmus method of Gumlich, and coercive force by means of a compensated magnetometer. Brinell hardness was also determined. All these tests were made on specimens quenched from temperatures between 700 and 1020°C. (1290 and 1870°F.). Results are given in Fig. 60.

As may be seen, coercive force does not increase appreciably within the region of solid solution but increases rapidly when the

copper concentration reaches the immiscibility region; on further increase in copper content it reaches a maximum and then decreases slowly. The authors attributed these changes in the coercive force of the alloys in the immiscibility region to the

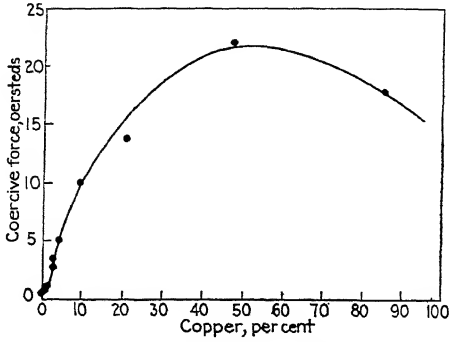


FIG. 60.—Coercive force of iron-copper alloys. (*Kussmann and Scharnow.*[237,238])

strains produced on cooling by the copper-rich envelopes surrounding the iron-rich crystals. Magnetic saturation was found to decrease linearly with increase in copper content (Fig. 61). Alloys containing up to 1 per cent copper, *i.e.*, in which all the copper presumably is in solid solution (after quenching), did

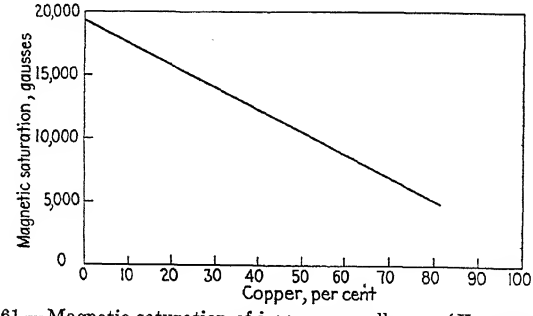


FIG. 61.—Magnetic saturation of iron-copper alloys. (*Kussmann and Scharnow.*[237])

not show any change in coercive force on quenching from different temperatures (Fig. 62). However, the alloys with higher copper content exhibited a decrease in coercive force and increased in hardness on quenching, owing to the increased solubility of copper at higher temperatures.

63. Influence of Copper on Magnetic Properties of Steel.—One of the earliest investigations of the magnetic properties of copper steels was made by Mme. Curie in 1898.[30] Her conclusion was that copper improves steel of the permanent-magnet type, for a quenched steel containing 0.87 per cent carbon and 3.9 per cent copper had a coercive force of 66 oersteds.

The effect of copper on the magnetic properties of commercial copper steels was also studied by Gerold.[287] His results indicated that the induction for a given magnetizing force decreases in proportion to the copper content, provided it does not exceed 2 per cent. The decrease in the induction due to 1 per cent copper, as taken from Gerold's curves, was for several magnetizing forces:

Magnetizing Force, Amp. Turns per Cm.	Decrease in Induction, Gausses
7.7	1100
25	350
50	250
100	150
300	100

Gerold also gave some results of his magnetic measurements of normalized copper steels:

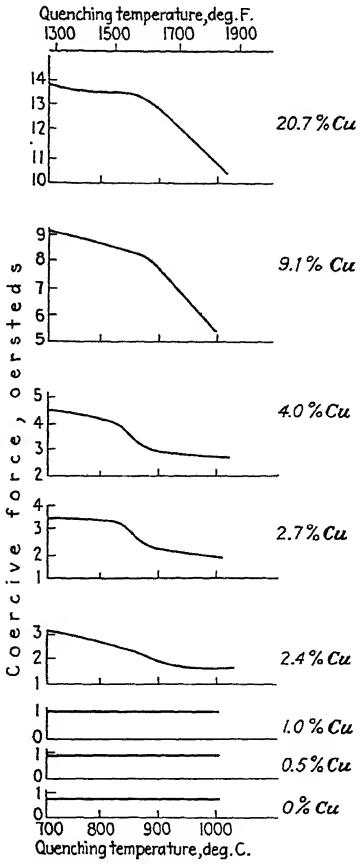


FIG. 62.—Coercive force of iron-copper alloys. (*Kussmann and Scharnow.*[237])

Composition, per cent				Induction, gausses, for a field strength of amp. turns per cm.			
C	Si	Mn	Cu	7.7	50	100	200
0.75	0.23	0.65	0.15	3,300	14,900	16,450	17,900
0.05	0.20	2.66	0.15	5,600	16,025	17,625	19,075
0.16	0.20	0.75	0.83	7,800	16,400	17,950	19,100

TABLE 25.—COMPOSITION OF STEELS USED BY STOGOFF AND MESSKIN[219]

Number	Composition, per cent			
	C	Si	Mn	Cu
1	0.87	0.06	0.14	1.19
2	0.76	0.16	0.21	3.03
3	0.69	0.06	0.31	4.81
4	1.11	0.07	0.17	1.42
5	1.07	0.08	0.22	3.25
6	1.03	0.09	0.14	5.07
7	0.74	0.16	0.34	1.41
07	1.22	0.12	0.15	1.27
K8	0.66	0.29	0.32	0.08
Ke10	0.92	0.22	0.49	0.03
K12	1.02	0.14	0.23	0.09
K10	1.06	0.19	0.19	0.07

TABLE 26.—MAGNETIC PROPERTIES OF QUENCHED COPPER STEELS*
(Compositions given in Table 25)

Number	Composition, per cent		Quenching temperature	Induction, (H = 600)	Residual induction, B_r, gausses	Coercive force, H_c, oersteds	$B_r \times H_c$ 10^{-3}
	Carbon	Copper					
Quenched in water							
1	0.87	1.19	770	1420	17,500	8,645	62.5	538.7
2	0.76	3.03	775	1425	17,822	9,447	58.3	550.8
2	0.76	3.03	800	1470	17,654	9,223	58.0	535.2
2	0.76	3.03	850	1560	16,266	8,556	60.5	516.6
3	0.69	4.81	800	1470	17,059	9,364	65.0	610.7
3	0.69	4.81	850	1560	17,292	9,030	61.0	550.8
3	0.69	4.81	900	1650	17,014	8,732	58.0	506.4
4	1.11	1.42	770	1420	16,130	8,372	64.6	544.1
5	1.07	3.25	770	1420	16,000	8,959	71.0	636.0
5	1.07	3.25	800	1470	15,505	7,660	69.0	528.0
6	1.03	5.07	770	1420	16,320	8,929	74.5	665.0
6	1.03	5.07	800	1470	14,720	7,866	78.0	613.6
7	0.74	1.41	775	1425	13,505	8,876	56.7	503.3
07	1.22	1.27	800	1470	15,000	7,759	65.0	504.8
Quenched in oil							
2	0.76	3.03	760	1400	17,043	8,942	58.9	526.7
2	0.76	3.03	800	1470	17,480	9,177	60.0	550.6
3	0.69	4.81	800	1470	16,570	8,702	61.0	530.8
3	0.69	4.81	850	1560	16,394	8,225	64.0	526.4
6	1.03	5.07	760	1400	15,912	8,781	59.0	518.1
6	1.03	5.07	800	1470	14,003	7,355	77.0	566.3
7	0.74	1.41	770	1420	16,850	8,994	60.0	539.1

* Stogoff and Messkin.[219]

Tempering at 600 to 650°C. (1110 to 1200°F.) slightly raised the induction values (200 to 300 gausses).

Stogoff and Messkin[219] investigated the suitability of high-carbon copper steels for permanent magnets. The magnetic

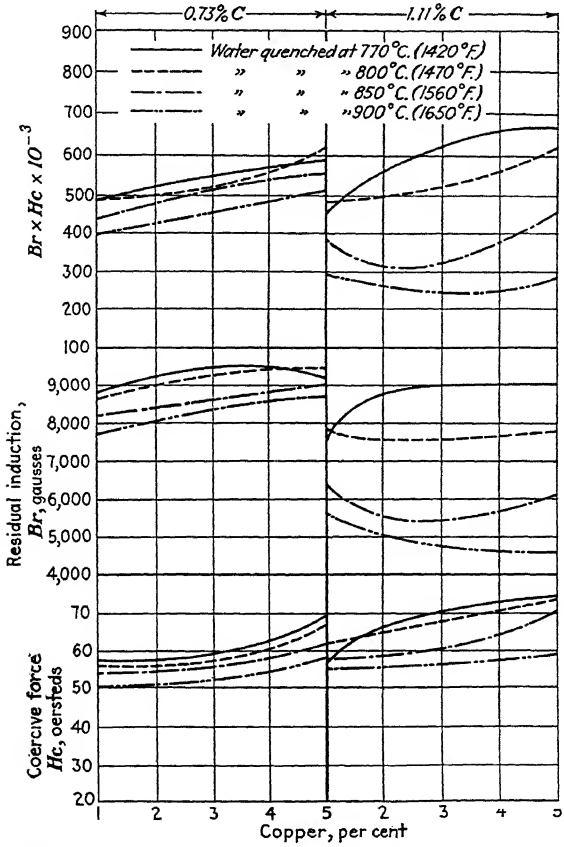


FIG. 63.—Magnetic properties of copper steels, quenched in water. (*Stogoff*

properties of eight copper steels, and of four carbon steels for comparison, were determined by a ballistic method using a maximum magnetizing force of 600 oersteds. The steels were melted in crucibles, the ingots forged into 16 × 16-mm. (0.630-in.) rods, and specimens 10 × 10 × 200 mm. (0.394 × 0.394 ×

7.875 in.) machined from these rods. The chemical compositions of the steels are given in Table 25.

The steels were quenched in oil and in water from 770, 800, 850, and 900°C. (1420, 1470, 1560, and 1650°F.). Some of the

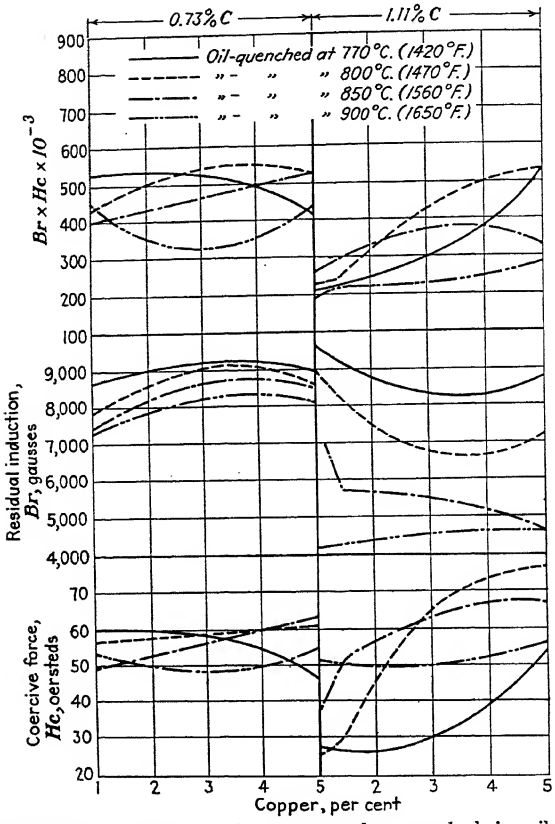


FIG. 64.—Magnetic properties of copper steels, quenched in oil. (*Stogoff and* .

results are given in Table 26. The tests of water-quenched specimens indicated that the coercive force of both hypo- and hyper-eutectoid steels increases with the copper content, while the residual induction remains constant or increases slightly (Fig. 63 and Table 26). The highest value of the product $H_c \times B_r$ was obtained in specimens quenched from 770 to 800°C. (1420 to 1470°F.).

Results obtained on oil-quenched specimens are more irregular, probably owing to the fact that they were not hardened uniformly throughout, as the microscopic examination showed. In most of the curves in Fig. 64 a definite turning point is observed at about 3 to 3.5 per cent copper. Oil-quenched samples all showed lower values of $B_r \times H_c$ than water-quenched, so that to obtain best magnetic properties in copper steels water quenching is recommended. The maximum product $B_r \times H_c$ was obtained by quenching from 800°C. (1470°F.).

In both the water-quenched and oil-quenched condition, steel containing 1.03 per cent carbon and 5.07 per cent copper was found to possess better magnetic properties than other steels investigated.

Tests made on annealed steels showed some tendency of copper to increase the coercive force of steel, as may be seen by comparing a copper steel with a copper-free steel:

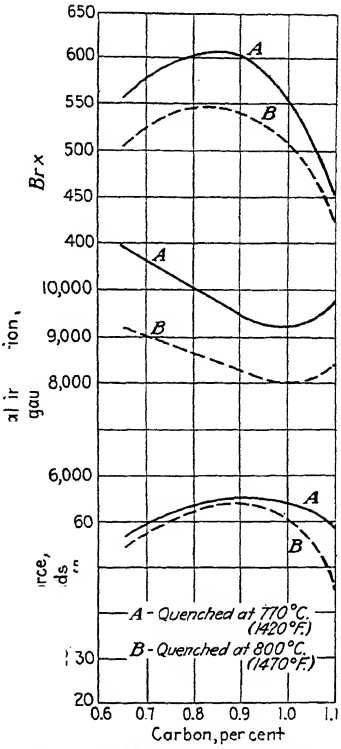


FIG. 65.—Magnetic properties of carbon steels. (*Stogoff and Mess-*

Steel	Composition, per cent		Coercive force, oersteds
	Carbon	Copper	
K8	0.66	0.08	10.5
3	0.69	4.81	15.5
K10	1.06	0.07	13.7
5	1.07	3.25	19.2

The magnetic properties of quenched copper steels should be compared with those of carbon steels shown in Table 27 and in Fig. 65.

TABLE 27.—MAGNETIC PROPERTIES OF CARBON STEELS*
(Compositions given in Table 25)

Number	Carbon, per cent	Quenching conditions						Magnetic properties			
		Quenching temperature		Quenching medium	Temperature of quenching medium		Time at hardening temperature, min.	$B_{max.}$, gausses	B_r, gausses	H_c, oersteds	$B_r \times H_c \times 10^{-3}$
		°C.	°F.		°C.	°F.					
K8	0.66	770	1420	Water	9	48	5	17,856	10,360	53.7	556.4
K8	0.66	800	1470	Water	15	59	5	17,134	9,165	55.2	505.9
Ke10	0.92	770	1420	Water	15	59	5	17,248	9,470	65.0	615.6
Ke10	0.92	800	1470	Water	15	59	5	16,241	8,395	65.0	545.7
K12	1.02	770	1420	Water	15	59	5	16,438	8,884	61.5	546.4
K12	1.02	800	1470	Water	15	59	5	15,162	7,785	64.3	500.6
K10	1.06	770	1420	Water	9	48	5	16,870	9,380	53.0	597.0
K8	0.66	850	1560	Oil	28	82	5	16,050	8,080	54.5	440.4
K8	0.66	900	1650	Oil	35	95	4	16,169	7,854	53.0	416.3
K12	1.02	800	1470	Oil	15	59	4	18,712	9,280	26.7	247.8
K12	1.02	850	1560	Oil	28	82	5	18,925	8,780	27.0	237.1

* Stogoff and Messkin.[219]

It may be seen that up to the eutectoid composition coercive force increases and residual induction decreases. Above the eutectoid composition residual induction remains practically constant, while coercive force decreases. The value $B_r \times H_c$ reaches a maximum at about 0.9 per cent carbon. It may be seen from Tables 26 and 27 and Figs. 62 to 65 that the coercive force of carbon steel is lower than that of copper steels of the same carbon content; the same can be said about the value $B_r \times H_c$. Residual induction, however, is either the same for both kinds of steel or is lower for copper steels.

64. Permanence of Copper Steels.—The decrease in magnetic flux on aging was found to be somewhat smaller in copper steels than in carbon steels but greater than in chromium-tungsten steels. Results obtained by Stogoff and Messkin showed that the flux of a steel containing 1 per cent carbon and 5 per cent copper decreases rapidly during the first 10 days and after 3 months remains practically constant.

Some results of artificial aging of quenched steels by cyclic heating and cooling (20 to 100°C. or 68 to 210°F.), repeated four times, are given below:[219]

Quenching temperature		Quenching medium	Flux		Decrease, per cent
°C.	°F.		Before aging	After aging	
770	1420	Water	4,032	3,896	3.3
800	1470	Oil	3,896	3,352	14.0
800	1470	Oil	3,873	3,715	4.1

65. Physical Constants.—Very little information is found in the literature on the effect of copper on the physical constants of iron.

Buchholtz and Köster[257] found that the transformation of a 5 per cent copper alloy (low-carbon steel) from the gamma to the alpha condition is accompanied by expansion, the expansion being greater the faster the rate of cooling. This, according to Buchholtz and Köster, is due to the fact that with faster cooling the alpha solution becomes more supersaturated with copper, since the absorption of copper is accompanied by increase in volume. The specific gravities were found to decrease with rising temperature of quenching. The lattice parameters of

alpha iron increase with the copper content retained in solution. As shown in Fig. 66, the specific gravities calculated from lattice parameters are in fair agreement with the experimentally determined values. Unfortunately, the reported values of lattice parameters are rather irregular, and extrapolation gives too low a value for pure iron. It must be remembered that these determinations have not been made on a pure iron-copper alloy but on a

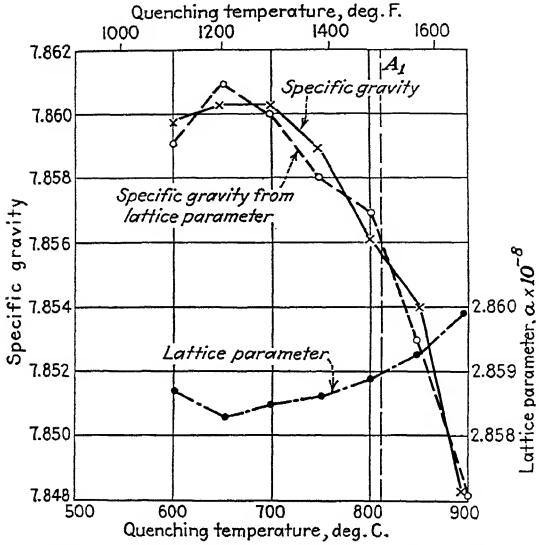


FIG. 66.—Influence of quenching temperature on the specific gravity and lattice parameter of a 5 per cent copper iron-copper alloy. (*Buchholtz and*

steel containing 5.0 per cent copper, 0.04 per cent carbon, 0.16 per cent manganese, 0.18 per cent silicon, 0.015 per cent phosphorus, and 0.039 per cent sulphur. It is thought, however, that the influence of these impurities is not very great, and the values for pure iron-copper alloys would be approximately the same.

Brown[51] made some determinations of densities and specific volumes of some steels with varying carbon and copper content. He concluded that, if the values are corrected for the presence of carbon, manganese, and aluminum, it will be found that the effect of adding up to 1.6 per cent copper to iron is to diminish slightly the specific volume of the alloys; further addi-

tions of copper do not seem to have any appreciable effect. The results obtained by Brown are given below:

Composition, per cent				Density	Specific volume	
C	Mn	Al	Cu		Observed	Calculated
0.68	0.36	...	1.59	7.8354	0.12763	0.12878
0.59	0.32	...	2.50	7.8366	0.12761	0.12837
0.17	1.04	...	2.87	7.8470	0.12744	0.12708
0.04	0.16	1.0	3.75	7.7479	0.12907	0.12905

Campbell, in a discussion of a paper by Norbury,[101] gave the value of 7.8 as the computed density for an alloy with 1 per cent copper and 99 per cent iron, and 8.9 for an alloy with 99 per cent copper and 1 per cent iron.

No data were found on the influence of composition on the specific heat of pure iron-copper alloys. However, it was stated[51] that when large amounts of carbon are present copper has no effect on the specific heat of iron.

D. CARBURIZING AND NITRIDING PROPERTIES

Although copper is not added to commercial steels intended for case hardening either by carburizing or by nitriding, some data on the influence of copper in such steels are available.

66. Case-carburizing Properties of Iron-copper Alloys.—The effect of copper on carburizing properties of iron was investigated by Smith.* His specimens were carburized at 900°C. (1650°F.) in a mixture of barium carbonate and charcoal. Chemical composition and the depth of case obtained in 4 hr. are shown below.

Composition, per cent		Depth of case, inches
Copper	Silicon	
1.10	0.192	0.059
2.13	0.154	0.052
3.04	0.114	0.055

It can be seen that copper within the limits investigated had very little effect on the depth of carburization. Smith observed

* Unpublished report by C. S. Smith of the American Brass Company.

that the high-copper specimens had somewhat irregular cases and attributed this irregularity to the formation of a film of copper beneath the oxide scale, tending to prevent carburization. His experiments also showed that the copper film is not sufficient to prevent carburization completely, although in every instance a much thinner case was obtained on alloys containing copper when they were given a scaling treatment before carburization.

67. Nitriding Properties of Copper Steels.—Nakayama[211] stated that elements which form stable nitrides (Al, Si, Ti, Cr) accelerate nitrogenation and that the maximum nitrogen content is attained in 1 hr. at 500°C. (930°F.). With elements which form no stable nitrides (as Cu, Ni, and Co) the maximum nitrogen content is obtained at 600°C. (1110°F.). Manganese forms a stable nitride and makes the nitrogen content larger, showing the maximum at 600°C. (1110°F.).

Coffman[315] investigated the nitriding properties of pure iron and several iron-copper alloys. The composition and average gain in weight after nitriding of the copper-bearing and of two copper-free alloys for comparison are given in Table 28.

TABLE 28.—NITROGEN ABSORPTION—AVERAGE GAIN IN WEIGHT*

Alloy	Composition, per cent			Temperature of maximum absorption		Average gain in weight at temperature of nitriding, g.			
	Cu	Mo				500°C. (930°F.)	600°C. (1110°F.)	700°C. (1290°F.)	800°C. (1470°F.)
1	0.04			700	1290	0.0242	0.1020	0.1250	0.0344
13	0.18			600	1110	0.0233	0.0347	0.0206	0.0134
11	0.12	0.82		600	1110	0.0225	0.0392	0.0147	0.0137
24	0.14	0.70		600	1110	0.0268	0.0535	0.0404	0.0122
12	0.10	0.75	0.87	600	1110	0.0224	0.0398	0.0209	0.0264
23	0.07	0.62	0.79	600	1110	0.0226	0.0484	0.0306	0.0282

* Coffman.[315]

The alloys were prepared from electrolytic iron and copper, annealed at 925°C. (1700°F.), air cooled, then annealed at 760°C. (1400°F.) and cooled in the furnace. Samples 0.1875 × 0.25 × 1 in. were nitrided for 4 to 24 hr. at temperatures from 500 to 800°C. (930 to 1470°F.).

The results indicated that pure iron absorbed more nitrogen than any of the alloys investigated. The maximum nitrogen absorption by iron-copper-carbon alloys was found to occur at 600°C. (1110°F.). Molybdenum added to copper-bearing alloys was found to have little effect on nitrogen absorption (if any, it decreased the absorption). The maximum hardness in the iron-copper-carbon alloys was found to coincide with the maximum absorption.

Some of the numerical values leading to these conclusions are given in Table 29. By comparing the effect of various elements on the maximum absorption, it will be seen that alloys of iron and copper absorb less nitrogen than the alloys of iron and aluminum or molybdenum, or iron containing both of these elements.

TABLE 29.—MAXIMUM NITROGEN ABSORPTION AND MAXIMUM AVERAGE HARDNESS OF SOME ALLOYS OF IRON*

Alloy	Composition, per cent					Maximum gain in weight, grams	Maximum hardness (Vickers)
	C	Cu	Al	Mo	Ni		
1	0.04	....	....	....	....	0.1250	403
4	0.04	....	1.80	0.85	....	0.1154	439
2	0.01	....	....	1.02	....	0.0929	467
15	0.10	....	2.86	....	....	0.0921	776
16	0.12	....	2.86	0.88	....	0.0916	857
9	0.06	....	....	....	0.98	0.0591	235
24	0.14	0.70	....	....	....	0.0535	411
23	0.07	0.62	....	0.79	....	0.0484	543
12	0.10	0.75	....	0.87	....	0.0398	329
11	0.12	0.82	....	....	....	0.0392	209
13	0.18	....	....	....	....	0.0347	187

* Coffman.[315]

E. AUTHORS' SUMMARY

1. Alloys of iron and copper may be divided into three classes: (*a*) Low-copper alloys. These are homogeneous solid solutions of copper in iron. (*b*) High-copper alloys—homogeneous solid solutions of iron in copper. (*c*) Intermediate alloys. These are heterogeneous alloys consisting of two metallographic constituents: one, iron-rich solid solution, and the other copper-rich solid solution.

2. The structure of pure or commercial iron is little affected by addition of small amounts of copper. Copper apparently

does not segregate and does not affect the grain size of pure iron. In the alloys containing large amounts of copper, the copper which exceeds the solubility limits separates out as a copper-rich constituent, epsilon, either in the form of small or large particles or as a network surrounding the ferrite grains, depending on the amount of copper present.

3. Iron supersaturated with copper and copper supersaturated with iron are subject to precipitation hardening at elevated temperatures whereby a constituent in excess of the solubility limit at given conditions is thrown out of solution. The condition of supersaturation in the iron-rich alloys is obtained by ordinary air cooling without drastic quenching.

4. Aside from the appearance of cementite, the microstructure of copper steels differs slightly from that of carbonless alloys as a consequence of the decreased solubility of copper in iron with increasing carbon content. For example, the separation of the epsilon phase from austenite will take place in steel at a lower copper concentration than in wrought or ingot iron, because carbon decreases the solubility of copper in iron.

5. The microstructure of rolled or forged steels with low copper does not differ appreciably from that of carbon steels, as far as the constituents are concerned. Rolled high-carbon, high-copper steels show extremely fine pearlite, sorbite, and martensite. Annealing these steels produces marked changes and causes the coalescence of the copper-rich constituent.

6. High-carbon, high-copper steels consist of martensite and austenite, or of martensite and troostite, when quenched from high temperatures or from temperatures just above the transformation temperatures respectively.

7. The amount of carbon in the eutectoid is not changed by the addition of copper.

8. Copper lowers the critical points of steel. The degree of lowering depends on the state of the alloy before cooling, the maximum heating temperature, and the rate of cooling.

9. The electric and magnetic properties of iron-copper alloys are greatly influenced by the addition of copper. With the same copper content the variations in the properties of steels depend on the amount of copper retained in solution or precipitated. The electric resistance of thoroughly annealed alloys increases as the copper concentration increases up to 0.4 per cent; above this concentration it decreases as the copper content increases.

The resistance of quenched steels increases with the copper content up to the limit of solubility, the magnitude of the increase depending on the amount of copper dissolved in gamma iron.

10. Copper decreases the magnetic permeability of iron. Annealing at 675°C. (1245°F.) improves permeability. Annealing at 1000°C. (1830°F.) or quenching from 900°C. (1650°F.) has only a very slight effect.

11. The coercive force of iron does not increase to any appreciable extent within the region of solid solution but increases rapidly when the copper concentration reaches the immiscibility region. Alloys containing up to 1 per cent copper do not show any change in coercive force on quenching from different temperatures. Quenching, however, increases the coercive force of alloys of higher copper content.

12. Fairly good permanent magnets can be made from copper steels.

13. The loss of magnetism of copper-steel magnets on aging is slightly smaller than for carbon-steel magnets and slightly greater than for chromium-tungsten magnets.

14. Copper has very little effect on the carburizing properties of iron. Some irregularities in the case may be caused by the protective action of the copper film which may be formed under any scale that may be present.

15. Copper apparently increases somewhat the depth of penetration of nitrogen in the nitriding of steels, although not to the same degree as molybdenum or aluminum.

CHAPTER VI

PRECIPITATION HARDENING OF COPPER STEELS

The Precipitation-hardening Process—Influence of Precipitation Hardening on Mechanical Properties—Influence of Precipitation Hardening on Physical Properties—Authors' Summary

The iron-copper equilibrium diagram (Fig. 18, page 33) shows that the solubility of copper in alpha iron (ferrite) decreases with decreasing temperature; this behavior would indicate that iron-rich alloys should be amenable to a precipitation-hardening treatment. As is generally accepted, precipitation hardening is brought about by first obtaining a supersaturated solid solution by cooling at a rate that will not permit the breakdown of the solution and then allowing precipitation from the solution to take place at a temperature at which the precipitated particles will be very small. The simplest explanation of the hardening brought about by precipitation is that numerous very small particles formed during precipitation obstruct slip by purely mechanical means and thereby increase hardness. Such a simple explanation, however, is not adequate for explaining all phenomena accompanying hardening, and it is entirely possible that the hardest "precipitation-hardened" material is one that is in some intermediate, but little understood, condition between a homogeneous solid solution and a mixture of the two phases. Although the term "precipitation hardening" suggests that hardening can be attributed to the precipitation of discrete particles, it is well to use it with the reservation that it often refers to the early stages of precipitation or a rearrangement of atoms prior to actual precipitation. A loosely synonymous term is "aging" or "age hardening," but speaking of "aging" at a temperature of 500 or 600°C. (930 or 1110°F.) is difficult to justify.

The ease of producing a supersaturated solid solution varies greatly from one system to another. In many alloys it is necessary to quench even a comparatively small section of the material in a liquid in order to produce a supersaturated solution that will subsequently harden by holding at a suitable temperature. In copper irons or steels the copper is not precipitated on compara-

tively slow cooling, and instead of quenching in a liquid being necessary it suffices to cool in air in order to produce the required solution of copper in iron. In fact, the necessary rate of cooling is so low that sections several inches in diameter can be hardened throughout by simply cooling in air and then reheating to a temperature in the neighborhood of 500°C. (930°F.).

As will be brought out in more detail below, precipitation hardening of iron-base alloys containing copper brings about an appreciable increase in strength. The increased strength is naturally accompanied by some loss in ductility, but the ductility of precipitation-hardened steels compares favorably with that of quenched and tempered carbon or the well-known low-alloy steels of comparable strength.

The purpose of the present chapter is to show how properties of iron-copper alloys may be varied by heat treatments and the treatments necessary to bring about precipitation hardening. More information on the mechanical properties of copper irons and steels will be found in subsequent chapters.

A. THE PRECIPITATION-HARDENING PROCESS

In the majority of precipitation-hardenable alloys hardening occurs when a metallic compound is precipitated from the supersaturated solid solution; in iron-copper alloys the "hardening particles" are copper, *i.e.*, copper containing a small amount of iron in solution and designated as epsilon phase in Chapter II. If hardening can be attributed to purely mechanical means, as is assumed here for simplifying the discussion, the iron-rich matrix is hardened by the comparatively soft particles of copper.

68. Studies of Precipitation Hardening.—Kinnear, as is shown by U. S. Patent 1,607,086 of November 16, 1926, and a journal article[291] that appeared in 1931, noted precipitation hardening in copper steels, but he made no extended investigation of the phenomenon. He found that low-carbon normalized steels containing 1 per cent copper increased in strength and hardness when reheated to a temperature in the neighborhood of 540°C. (1000°F.).

An article by Nehl,[267] published in 1930 (also U.S. Patent 1,835,667 of December 8, 1931), described an extensive study of precipitation-hardening phenomena in copper steels and showed just how the maximum strength and hardness could be produced by a precipitation treatment. An article by Buchholtz and

Köster,[257] also published in 1930, contained additional data on precipitation hardening of copper steels as well as data on the properties of copper-chromium steels.

A dissertation by Baumgardt,[278] published in 1931, contained much interesting information on precipitation hardening of copper steels; some of Baumgardt's results will be found in Nehl's article.

Many data on precipitation hardening of copper steels were reported by Smith and Palmer[378] in 1932, and additional results of these workers were made available for this monograph through the courtesy of the Anaconda Copper Mining Company and the Copper and Brass Research Association. Lorig and MacLaren of Battelle Memorial Institute also obtained experimental data on the properties of copper irons and steel; their results were made available through the courtesy of the Copper and Brass Research Association.

It may be well to mention at this point that in all cases copper steels rather than substantially pure iron-carbon alloys have been used in studying precipitation hardening. Many of the steels, however, contained less than 0.1 per cent carbon, and, as a fair approximation, steels of a really low carbon content may be considered as substantially pure iron-copper alloys in so far as their response to precipitation hardening due to copper is concerned. As is shown by data given below, within certain limits at least, variation in the carbon content of steels has little influence on the change in mechanical properties brought about by precipitation of copper from the supersaturated solid solution.

In a report prepared in 1922, Bird, of the Bethlehem Steel Company, gave some data which, according to our present understanding of copper steels, show precipitation-hardening effects in copper steels containing 0.30 per cent carbon and as much as 3 per cent copper. Some of Bird's results are given in Chapter VIII.

69. Amount of Copper Soluble in Alpha Iron.—In order to be susceptible to precipitation hardening an alloy must contain more copper than is soluble at ordinary temperature. In most alloys the hardness increase on precipitation increases as the amount of solute increases up to the limit of saturation at the temperature of solution treatment—usually the quenching temperature. In the alloys under consideration, however, the maximum hardening effect is reached at approximately 1.5 per cent copper; according

to Smith and Palmer, further increase in copper actually decreasing the hardness increase resulting from precipitation. This is somewhat unexpected, for at the eutectoid temperature about 3.5 per cent copper is soluble in alpha iron, according to Buchholtz and Köster. Furthermore, electric resistance, lattice parameter, and density determined by Buchholtz and Köster have shown that, if an alloy containing 5 per cent copper is quenched from the gamma field, the gamma phase is transformed to alpha, yet none of the copper is precipitated, thus producing alpha iron containing 5 per cent copper when a maximum of 3.5 per cent is soluble under equilibrium conditions at any temperature. If 5 per cent copper can be held in forced solid solution in alpha iron by quenching from the gamma field, it may be possible to have as much as 8 per cent by quenching an alloy containing more copper from a temperature near 1100°C. (2010°F.), point *L* in Fig. 18. Yet the available information indicates that, contrary to expectations, the hardness increase on heating such a material to the precipitating temperature is no greater than for a 1.5 per cent copper alloy. As the copper content is increased further, the hardness of the quenched alloys increases but the change in hardness produced by heating to the precipitation temperature becomes negligible.

The best information available on the solubility of copper in iron at ordinary temperature is based on the response to a precipitation-hardening treatment; an alloy which contains just sufficient copper to respond to the treatment should be very close to the solubility limit. This limit was placed at 0.6 per cent by Nehl, 0.7 per cent by Smith and Palmer, and at 0.4 per cent by Buchholtz and Köster. It is believed that the lowest value should be accepted, but that it can be assumed that marked precipitation hardening occurs only when the highest value (0.7 per cent) is exceeded. This would mean that iron-copper alloys containing more than 0.7 per cent copper can be measurably hardened by a precipitation treatment and that the magnitude of the hardening effects increases until the copper content reaches 1.5 per cent.

70. Obtaining a Supersaturated Solid Solution.—The solubility of copper in alpha iron, according to Buchholtz and Köster, is 0.4 per cent at temperatures of 600°C. (1110°F.) and below. In order to obtain some idea of the amount of copper which can be held in supersaturated solution at ordinary tem-

peratures, these investigators studied a steel of the following composition:

Element	Percentage
Carbon	0.04
Silicon	0.18
Manganese	0.16
Phosphorus	0.015
Sulphur	0.039
Copper	5.0

This steel was maintained at 600°C. (1110°F.) for 24 hr. in order to precipitate and agglomerate the copper not soluble at

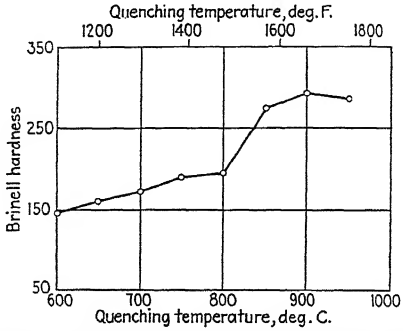


FIG. 67.—Hardness of a 5 per cent copper iron-copper alloy quenched from the indicated temperatures. (*Buchholtz and Köster.*[257])

low temperatures. Samples were then heated to temperatures of from 600 to 950°C. (1110° to 1740°F.) and quenched, after which their Brinell hardness was determined. The results are shown in Fig. 67. As the quenching temperature was increased above 600°C. (1110°F.), the hardness increased because of the greater amount of copper held in solid solution. The discontinuity of the curve between 800 and 850°C. (1470 and 1560°F.) possibly indicates that much more copper is held in solution when the steel is quenched from the gamma field than when it is quenched from just below the gamma field. On the other hand, the increased hardness may result from the gamma-alpha transformation alone. Samples quenched from the different temperatures were reheated for periods of 1 hr. at different temperatures and the hardness values shown in Fig. 68 determined. No increase in hardness resulted from reheating the alloy quenched from 600°C. (1110°F.). But the hardness of alloys quenched from higher temperatures

increased on reheating and, in general, the hardness increase became greater as the temperatures from which the alloys were quenched became higher. The hardness increase when compared with increase in quenching temperature is rather irregular, and it is hardly safe to interpret these curves as proving that the amount of hardening on precipitation increases as the quenching temperature is increased from 700 to 900°C. (1290 to 1650°F.); certainly a real hardness increase occurred in the sample quenched

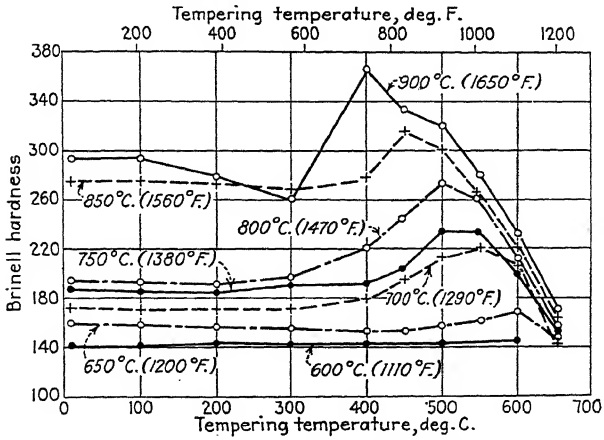


FIG. 68.—Hardness of samples of a 5 per cent copper iron-copper alloy, quenched from the temperatures shown on the curves and reheated to the indicated temperatures for periods of 1 hr. (*Buchholtz and Köster.*[257])

from the lower temperature. While discussing Fig. 68, it may be well to call attention to the fact that it indicates, for the reheating periods used, the reheating temperature which produces maximum hardness decreases with increased quenching temperature.

Nehl found that the presence of 1.3 per cent copper in low-carbon steel produced as great a precipitation-hardening effect as larger amounts of copper and assumed that only 1.3 per cent copper was held in solution on cooling in air.

In order to determine the cooling rate necessary to hold the copper in solution, Nehl heated specimens of a steel to 900°C. (1650°F.), cooled them at different rates, reheated each specimen to 525°C. (975°F.) for 2 hr., and then determined the tensile strength. The steel contained 0.12 per cent carbon and 0.85 per cent copper. Figure 69 shows the increase in strength resulting from reheating, plotted against the time required to

cool from 900°C. (1650°F.) to ordinary temperature. Maximum increase in strength occurred in those samples which were cooled in 6 hr. or less, indicating that no copper was precipitated from these specimens on cooling to ordinary temperature. As the cooling time exceeded 6 hr., the strength increase became smaller until the sample cooled in 72 hr. showed no hardness increase at all. Even cooling in 6 hr. is a comparatively slow rate, and the results indicate that precipitation of copper would not occur if sections several inches in diameter would be air cooled. Buchholtz and Köster (see Chapter XI) found that an air-cooled

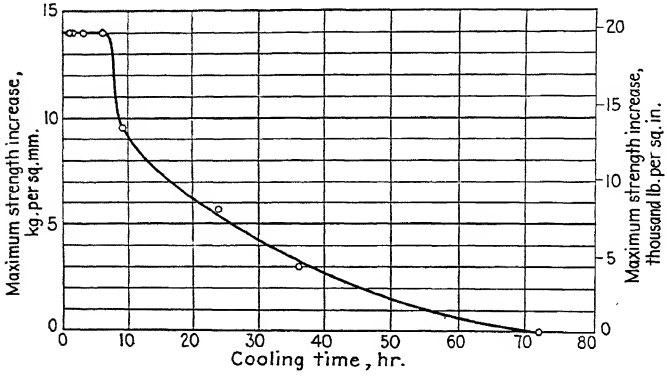


FIG. 69.—Increase in strength, as compared with untreated condition, on reheating samples of a 0.85 per cent copper alloy to 525°C. (975°F.) for 2 hr. after cooling from 900°C. (1650°F.) at different rates. (*Nehl.*[267])

section of a copper-chromium steel 300 mm. (11.8 in.) in diameter responded to the precipitation-hardening treatment.

In determining the cooling rates required to produce a supersaturated solid solution of copper in steel, Smith and Palmer used steels containing either 1 or 2 per cent copper and from 0.03 to 0.90 per cent carbon. Specimens of these steels were cooled from both 800 and 900°C. (1470 and 1650°F.) at nine different rates and then reheated for the necessary time at the temperature required to produce maximum hardening. As is shown by the many data and curves given in Smith and Palmer's paper, cooling through the precipitation range, in the neighborhood of 500°C. (930°F.), at the rate of 25°C. (45°F.) per min. suffices to keep at least 1 per cent copper in solution in low-carbon steels. The hardness increase on reheating did not begin to decrease until the cooling rate became less than 1.5°C. (2.7°F.)

per min., and some hardening occurred even after cooling at 0.4°C. (0.7°F.) per min. The presence of carbon tends to promote precipitation on cooling, but "precipitation will occur to a useful extent following cooling at a rate of 1.5°C. (2.7°F.) per min. (100°C. or 180°F. per hr.) and is not absent after cooling at 25°C. (45°F.) per hr." Quoting further from Smith and Palmer:

To obtain the best properties from copper steels *it is not necessary to quench.* An air cool, even of comparatively heavy sections, suffices to retain most of the copper in solution and to result in a considerable increase in hardness when the simple precipitation treatment is given.

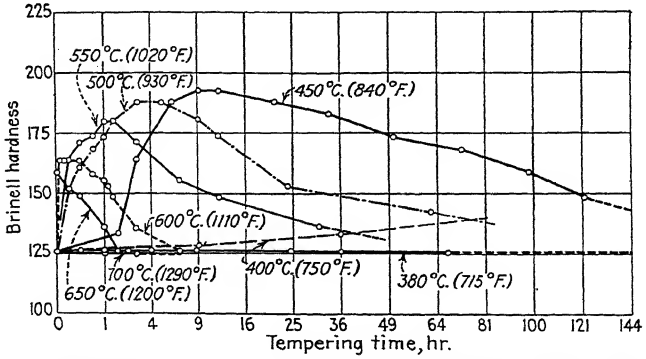


FIG. 70.—Hardness of a 1 per cent copper steel, reheated different times at temperatures shown.

71. Hardening by Reheating.—It is necessary to reheat the supersaturated solution of copper in iron to cause precipitation hardening. As in other alloy systems, the hardening effect depends both on the temperature to which the material is heated and the time it is held at this temperature. In studying the influence of time and temperature Nehl obtained the curves shown in Fig. 70 for a steel containing 0.08 per cent carbon and 1.01 per cent copper, which was presumably in the as-rolled condition. When this steel was held for as long as 120 hr. at 380°C. (715°F.) no change in Brinell hardness took place. When held at 400°C. (750°F.), however, the hardness gradually increased, which increase is very probably due to a partial precipitation of copper from the supersaturated solution. At higher temperatures the change in hardness occurred much more rapidly, and with increased time at temperature the hardness

rose to a maximum and then decreased. The greatest hardness increase took place on heating at 450°C. (840°F.) for 9 hr. At 500°C. (930°F.) the maximum hardness reached was less, but, as was to be expected, the greatest hardness increase occurred with a shorter time at temperature (4 hr.).

Figure 71, from Smith and Palmer, shows the hardness of samples of a normalized steel containing 0.06 per cent carbon and 1.06 per cent copper after having been reheated for different times at several temperatures. As in Nehl's experiments, the

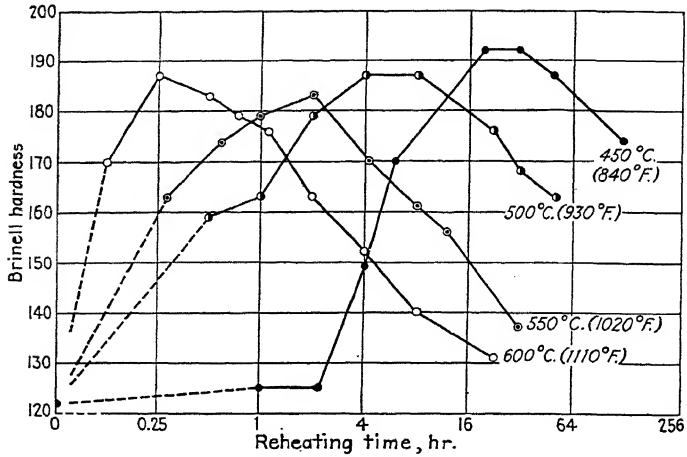


FIG. 71.—Hardness of a normalized steel containing 0.06 per cent carbon and 1.06 per cent copper, after reheating as indicated. (*Smith and Palmer.*[378])

maximum hardness was reached on reheating at 450°C. (840°F.), and the hardness reached at 500°C. (930°F.) was only slightly less. As a practicable heat treatment, which produces nearly the greatest possible hardness but does not require an unreasonably long time, Smith and Palmer recommended reheating for 4 hr. at 500°C. (930°F.).

Results obtained by Lorig and MacLaren with plain copper steels and by Buchholtz and Köster with copper-chromium steels also showed that reheating for 4 hr. at 500°C. (930°F.) is an effective and desirable treatment.

For a reheating time of 1.5 hr. Rädeker[369] found that the greatest increase in hardness occurred for a temperature of 475°C. (885°F.).

72. Hardening by Interrupted Cooling.—Baumgardt[278] found that by cooling rapidly from 930 to 525°C. (1705 to 975°F.) and holding at the latter temperature for 1.5 hr. the same hardness was produced as by cooling to room temperature and then heating to 525°C. (975°F.). In order to suppress precipitation-hardening ability completely it was necessary to hold the material at 640°C. (1185°F.) for 6 hr. Smith and Palmer also found that it was not necessary to cool to ordinary temperatures and then reheat in order to produce precipitation hardening; it is only necessary

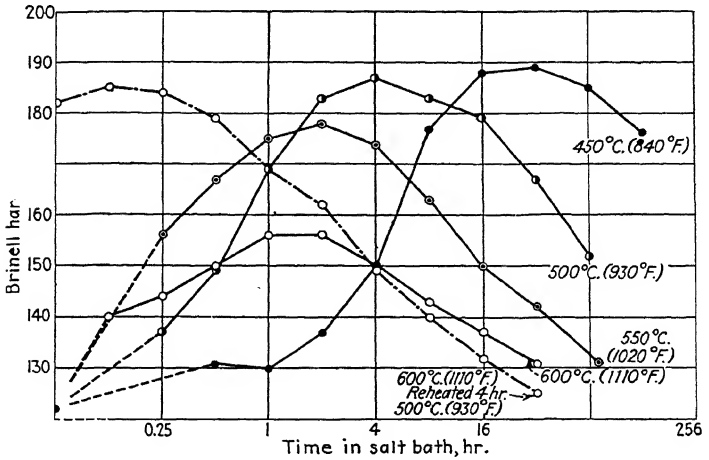


FIG. 72.—Hardness of a steel containing 0.06 per cent carbon and 1.06 per cent copper, cooled rapidly from 865°C. (1590°F.) to different temperatures and then held for different times. (*Smith and Palmer.*[378])

to cool to the precipitation temperature and hold at this temperature for the required time. This is shown by Fig. 72, which gives Brinell hardness values of the steel referred to above after quenching from 865°C. (1590°F.) into a salt bath held at constant temperatures and keeping in the salt bath for different times. Comparison with Fig. 71 will show that for temperatures of 450, 500, and 550°C. (840, 930, and 1020°F.) the hardness values reached are the same as for cooling to ordinary temperature and then reheating. Tensile tests showed that the same properties resulted from the two types of treatment. For the two types of treatment the hardness change at 600°C. (1110°F.) was different. This difference was attributed to difference in nuclei formation as is outlined below. At the comparatively

high temperature of 600°C. (1110°F.) few nuclei are formed, but the rate of particle growth is great; relatively few and, therefore, large particles of copper are formed, which have little strengthening effect. If the material is first cooled below 600°C. (1110°F.) and then reheated, more nuclei are formed, and the hardness-time curve for 600°C. (1110°F.) is different. The dashed line in Fig. 72 shows the hardness-time curve of material cooled to 600°C. (1110°F.), then to ordinary temperature, and then reheated for 4 hr. at 500°C. (930°F.). The increase in hardness on reheating lends support to the suggestion that nuclei formation is of prime importance.

B. INFLUENCE OF PRECIPITATION HARDENING ON MECHANICAL PROPERTIES

Some of the data given above show the hardness increase brought about by precipitation hardening of low-carbon steels. Generally, hardening of this type results in increased strength as well as hardness and at the same time decreases ductility. The properties of a copper steel, even though it has been given a precipitation-hardening treatment, depend on the carbon content, and it will be convenient to distinguish between low-carbon steels and steels of higher carbon content, and to place the steels which do not quench-harden by any but the most drastic treatment in the former group and all others in the latter group.

73. Low-carbon Steels.—Iron-carbon, as well as iron-copper, alloys respond to a precipitation-hardening treatment, but carbon is precipitated on holding at room temperature, while copper is not precipitated at a temperature below 400°C. (750°F.), at least not for heating times of less than 100 hr. The quantity of carbon required for hardening by precipitation is very small, only a few hundredths of 1 per cent, and almost any commercial low-carbon iron responds to a precipitation-hardening treatment. The effects of carbon precipitation in low-carbon alloys are not superimposed on the effects of copper as is evident from Fig. 73 taken from Buchholtz and Köster.[257] This figure gives hardness values of an alloy containing 0.05 per cent carbon and 2.0 per cent copper, which was cooled at an intermediate rate from 930 to 680°C. (1705 to 1255°F.), quenched, and then given the "aging" treatments shown. At ordinary temperature and at 100°C. (210°F.) cementite* (Fe_3C) was precipitated and increased

* Other substances such as nitrides or oxides might also precipitate at these temperatures.

the hardness. As the temperature was raised to 200 or 300°C. (390 or 570°F.), the alloy was overaged with respect to cementite precipitation and the hardness decreased to the original value. As the temperature was raised to 400°C. (750°F.) and above, the copper began to precipitate, as is shown by the increased hardness. The two distinct peaks in the curve and the drop of the hardness to the original value between the peaks show that the effects of precipitation of carbon and copper are not superimposed.

Figure 74, from Nehl,[267] shows the tensile properties and impact resistance of a rolled steel containing 0.08 per cent carbon

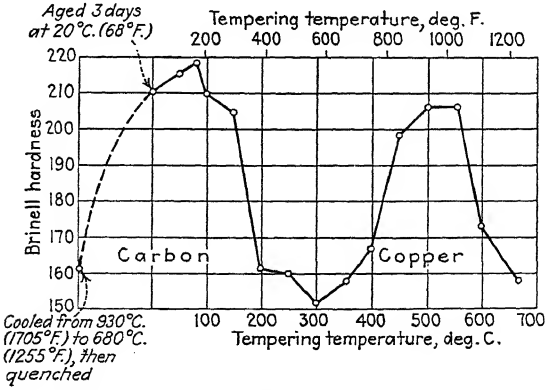


FIG. 73.—Hardness of a steel containing 0.05 per cent carbon and 2.0 per cent copper, quenched from 680°C. (1255°F.) and then reheated to different temperatures for a period of 30 min. (*Buchholtz and Köster.*[257])

and 1.01 per cent copper after reheating to different temperatures. On reheating to 500 or 550°C. (930 or 1020°F.) the tensile strength and yield strength were increased by 20,000 lb. per sq. in. This increase in strength was accompanied by a decrease in elongation, reduction of area, and notch-impact resistance.

The properties of normalized and reheated specimens of a steel containing 0.04 per cent carbon and 1.06 per cent copper, as reported by Smith and Palmer,[378] are shown in Fig. 75. On reheating to 500°C. (930°F.) for 4 hr. the increase in tensile strength and yield strength was between 20,000 and 30,000 lb. per sq. in. Impact-resistance values of a steel containing 0.08 per cent carbon and 1.04 per cent copper are shown in Fig. 76. These curves show that precipitation hardening appreciably decreases the notched-bar impact resistance and that the treat-

ment which produces maximum hardness produces the minimum impact resistance.

The reported data on the influence of precipitation hardening on the mechanical properties of low-carbon steel are in agreement in indicating that precipitation hardening of steels containing

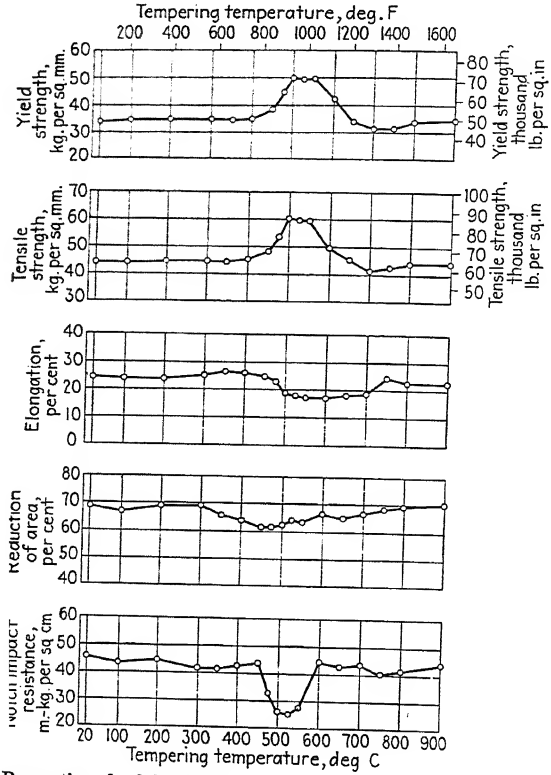


FIG. 74.—Properties of a 0.08 per cent carbon, 1.01 per cent copper steel, rolled and then reheated to the temperatures shown. (*Nehl.*[267])

1 per cent or more copper increases the tensile strength and yield strength by at least 20,000 lb. per sq. in.

74. Steels of Higher Carbon Content.—As was shown above, precipitation-hardening effects of copper and carbon are not superimposed. However, on reheating steels containing sufficient carbon to be hardened by rapid cooling (martensitic hardening) the effects of softening by tempering and hardening by precipitation

may be superimposed. Thus, even though a steel is hardened by precipitation of copper, it may be softer after the precipitation treatment than after rapid cooling. The superimposition of softening due to tempering and hardening due to precipitation of copper will be evident in some of the data given in Chapter VIII.

Figure 77, from Smith and Palmer,[378] shows the properties of a steel containing 0.56 per cent carbon and 1.03 per cent copper

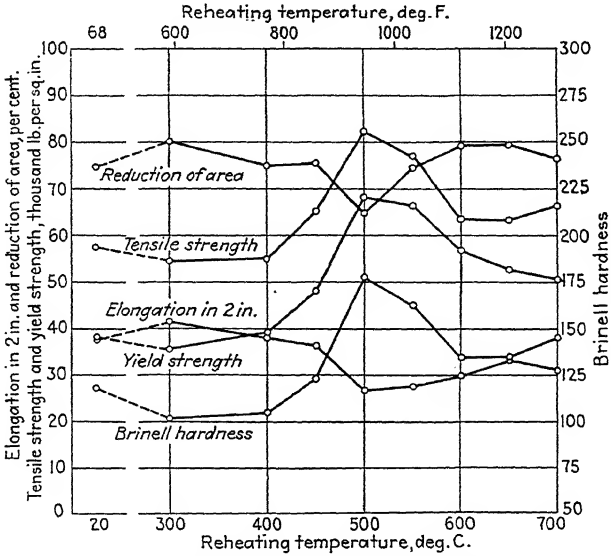


FIG. 75.—Properties of a steel containing 0.04 per cent carbon and 1.06 per cent copper, normalized at 865°C. (1590°F.) and then reheated for 4 hr. at the temperatures shown. (*Smith and Palmer.*[378])

after having been normalized and then reheated for a period of 4 hr. to different temperatures. Comparison of this illustration with Fig. 75 shows that almost the same increase in strength was produced in this steel by precipitation hardening as in a steel containing only 0.04 per cent carbon. The strength after any treatment is, of course, greater for the steel of higher carbon content. It, therefore, appears that both the tensile strength and the yield strength of a normalized copper steel containing up to 0.55 per cent carbon can be increased by 20,000 lb. per sq. in. by simply reheating for 4 hr. at 500°C. (930°F.), the increase in

strength being practically independent of carbon content within this range.

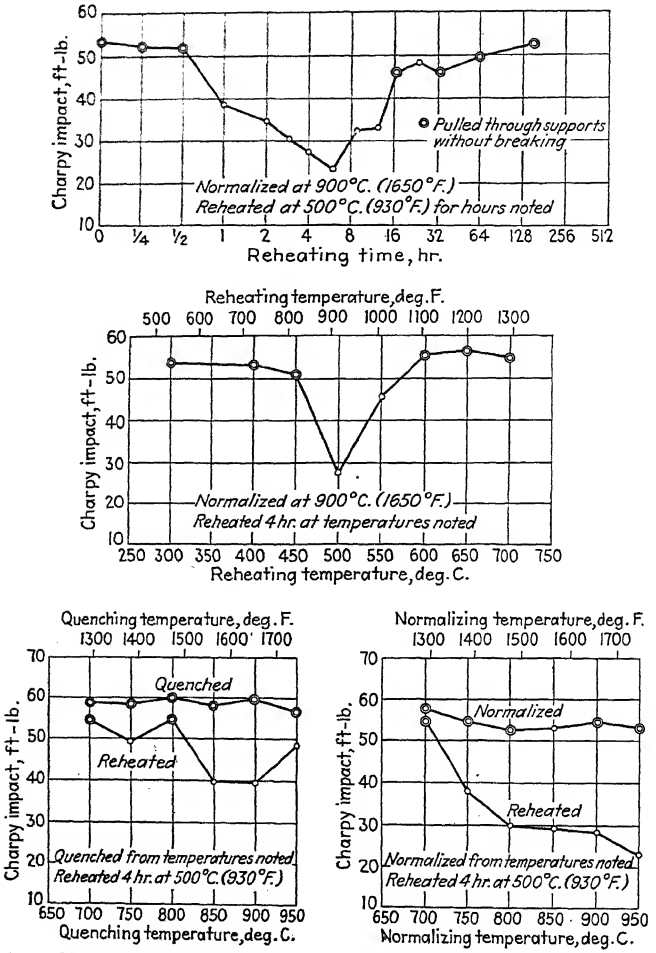


FIG. 76.—Charpy impact resistance of a steel containing 0.08 per cent carbon and 1.04 per cent copper. (*Smith and Palmer.*[378])

Lorig and MacLaren found that by precipitation hardening the Brinell hardness of rail steels containing between 0.8 and 0.9 per cent carbon and 1 per cent copper could be increased from 20 to 25 points and the yield strength by 10,000 lb. per sq. in.

75. Steels Containing an Alloying Element in Addition to Copper.—Table 30 from Smith and Palmer[378] gives mechanical properties of steels containing an alloying element in addition to copper. According to these data, the addition of silicon, manganese, vanadium, zirconium, chromium, nickel, aluminum, titanium, molybdenum, tungsten, cobalt, phosphorus, or arsenic

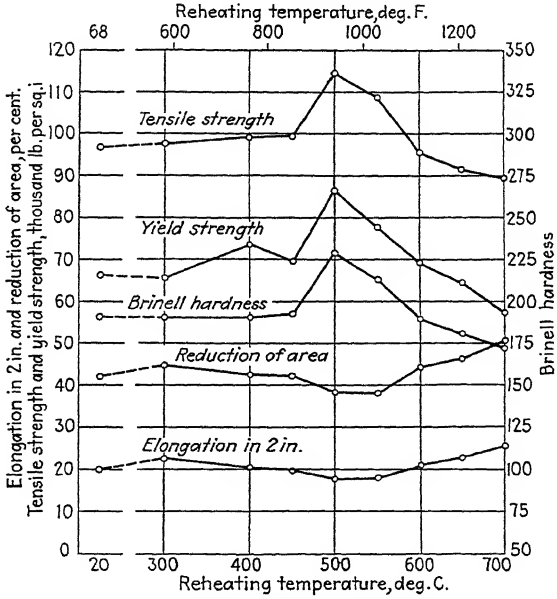


FIG. 77.—Mechanical properties of a steel containing 0.56 per cent carbon and 1.03 per cent copper, normalized at 810°C. (1490°F.) and then reheated for 4 hr. at the temperatures shown. (*Smith and Palmer.*[378])

does not appreciably influence the response of copper steels to a precipitation-hardening treatment, although the properties of the steel may be modified by the addition of the alloying element. It, therefore, appears that the addition of copper to almost any low-alloy steel of low- or medium-carbon content yields a material whose strength in the normalized condition can be increased by approximately 20,000 lb. per sq. in. by a precipitation-hardening treatment.

Buchholtz and Köster[257] also showed that copper-chromium steels can be hardened by a precipitation-hardening treatment. Some of their data are given later in the discussion of complex alloys.

TABLE 30.—PRECIPITATION HARDENING OF STEELS CONTAINING COPPER AND ONE OTHER ALLOYING ELEMENT*

Part I. Composition, Treatment, and Hardness

Alloy number	Composition, per cent			Normalizing temperature		Brinell hardness as normalized and after reheating 4 hr. at temperature noted				
	Cu†	Other elements				Normalized	400°C. (750°F.)	450°C. (840°F.)	500°C. (930°F.)	550°C. (1020°F.)
658		0.03†	1.11 Si	950	1740	115			185	
				800	1470	111			171	
659	1.05	0.03†	1.97 Si	950	1740	131			196	
				800	1470	134			186	
661	2.05	0.03†	1.01 Si	950	1740	141			240	
				800	1470	121			198	
662	2.12	0.03†	2.00 Si	Q 950	1740	150			241	
				Q 800	1470	138			213	
664	3.05	0.03†	0.96 Si	Q 950	1740	219			269	
				Q 800	1470	122			199	
665	3.08	0.03†	2.04 Si	950	1740	200			[illegible]	
				800	1470	148			213	
666	1.09	0.03†	2.92 Si	950	1740	174			219	
				800	1470	172			224	
951		0.081	1.02 Mn	865	1590	116		117	118	116
952	1	0.092	1.19 Mn	865	1590	139	...	169	187	172
953	1	0.093	.88 Mn	865	1590	179	179	198	197	177
954	2	0.092	.91 Mn	865	1590	233	229	229	216	197
955	0	0.216	.30 Mn	865	1590	157		152	156	148
956	1	0.214	1.27 Mn	865	1590	175	...	185	209	181
957	1.	0.226	1.93 Mn	865	1590	230	230	237	229	209
958	2.	0.207	1.91 Mn	865	1590	307	300	286	255	229
959	4	0.213	1.91 Mn	865	1590	369	359	321	285	260
...	1.0	0.091	0.053 V			127		137	179	169
970	1.0	0.079	0.112 V	.....	.....	131		140	186	170
971	1.0	0.082	0.224 V	900	1650	136		141	187	179
972	2.0	0.083	0.223 V	900	1650	176		196	222	196
973	1.0	0.212	0.059 V			154		161	195	188
974	1.0	0.217	0.113 V	.....	.....	154		170	201	187
975	1.0	0.219	0.226 V	865	1590	163		174	210	198
976	1.0	0.483	0.227 V	865	1590	215		218	253	239
977	1.0	0.183	0.091 Zr	865	1590	147		156	197	186
978	1.0	0.106	1.13 Cr	900	1650	126		140	187	175
979	1.0	0.236	1.14 Cr	900	1650	175		185	222	207
980	1.0	0.092	3.50 Ni	865	1590	166		190	198	183
981	0.995	0.077	2.51 Ni	865	1590	154		170	196	179
982	2.01	0.086	2.52 Ni	865	1590	208	217	231	225	196
983	1.0	0.215	3.51 Ni	865	1590	195		212	219	202
984	1.0	0.215	2.54 Ni	865	1590	180		204	217	197
985	1.0	0.201	.01 Ni	865	1	163		180	205	195
1007	1.0	0.189	0. ... Al	865	1590	149		163	191	182
1008	1.0	0.176	0.934 Ti	865	1590	155		163	190	179
1009	1.0	0.242	0.983 Mo	900	1650	243		257	282	268
1010	1.0	0.227	0.920 W	900	1650	169		188	217	207
1011	1.0	0.215	3.56 Co	865	1590	163		172	215	197
1012	1.0	0.208	1.00 Co	865	1590	154		165	204	187
1164	1.22	0.257	0.210 P	900	1650					
1165	0.65†	0.08†	0.11† P	900	1650	[illegible]	[illegible]	[illegible]	152	143
1166	1.07	0.030	0.165 P	900	1650	135	137	179	195	179
1167	2.12	0.045	0.338 P	900	1650	212	218	246	241	211
1169	1.0†	0.08†	0.50† Sn	.....	....	161	166	196	185	170
1170	1.0†	0.08†	0.50† Sb	.....	....	143	143	170	179	156
1171	1.0†	0.093	0.307 As	900	1650	136	143	183	195	186

TABLE 30.—PRECIPITATION HARDENING OF STEELS CONTAINING COPPER AND ONE OTHER ALLOYING ELEMENT*

Part II. Tensile Properties

Alloy number	Properties as normalized				Properties after reheating 4 hr. at 500°C.			
	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.‡	Elongation in 2 in., per cent	Reduction of area, per cent	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.‡	Elongation in 2 in., per cent	Reduction of area, per cent
658	64,450	.....	27.0	66.9	87,650	.....	20.5	50.8
	62,250	.....	26.3	68.7	81,850	.....	8.3	4.9
659	65,900	.....	28.0	64.1	94,150	.....	14.5	23.7
	65,600	.....	26.3	60.7	86,400	.....	11.0	15.3
661	75,750	.....	32.0	70.4	114,350	.....	19.0	56.3
	66,450	.....	30.0	69.0	91,750	.....	22.0	60.3
662	76,100	.....	22.5	59.2	25,170	.....	1.3	0.9
	70,800	.....	27.3	63.5	88,700	.....	5.3	1.4
664	110,400	.....	16.3	51.8	125,750	.....	16.8	55.6
	68,000	.....	30.0	74.9	93,800	.....	22.3	64.5
665	112,800	.....	17.5	52.3	127,000	.....	6.3	8.3
	75,500	.....	28.5	61.2	101,850	.....	20.3	53.3
666	84,400	.....	23.3	59.1	85,400	.....	2.3	0.3
	83,800	.....	27.5	48.6	102,850	.....	9.5	8.2
951	63,150	42,650	40.0	75.6	63,150	42,800	40.0	75.5
952	72,800	49,650	37.0	72.4	92,200	77,650	29.0	68.8
953	97,900	51,500	27.5	54.1	99,550	78,650§	27.5	66.0
654	122,200	73,650	20.5	45.6	113,800	90,950§	24.5	61.4
955	82,850	57,250	33.0	69.7	81,900	56,800	33.3	69.3
956	90,750	69,150	30.3	64.0	104,100	86,550	26.5	61.5
957	130,900	69,400	17.0	30.7	121,750	97,350§	21.5	54.0
958	170,400	93,750	13.0	24.3	143,450	118,050§	18.5	51.2
959	198,700	109,100	11.8	23.2	158,100	132,150§	15.3	47.1
969								
970								
971	68,400	58,600	35.8	72.7	88,550	81,050	29.3	67.0
972	84,500	79,750	30.3	67.9	104,300	98,000	26.0	63.4
973								
974								
975	83,600	67,400	30.5	62.7	102,050	89,200	26.0	58.7
976	109,500	83,400	23.8	49.9	125,900	104,900	21.3	47.7
977	76,800	58,500	32.3	63.8	95,750	81,750	27.0	59.1
978	67,150	52,500	38.3	78.2	88,000	79,650	30.5	71.6
979	89,900	68,650	30.5	67.4	108,900	90,900	26.0	64.0
980	87,100	53,350	31.3	60.8	95,500	81,900	27.3	65.7
981	77,300	58,500	33.0	64.8	92,700	80,550	28.0	64.0
982	103,500	74,600	24.0	54.6	108,850	93,300§	25.0	59.8
983	102,200	62,000	24.5	48.1	108,750	93,500	24.8	55.6
984	92,200	68,650	28.3	57.0	104,750	90,650	25.3	57.1
985	84,150	65,100	30.0	59.4	102,400	86,050	25.0	55.5

TABLE 30.—PRECIPITATION HARDENING OF STEELS CONTAINING COPPER AND ONE OTHER ALLOYING ELEMENT.*—(*Part II Continued*)

Alloy number	Properties as normalized				Properties after reheating 4 hr. at 500°C.			
	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.‡	Elongation in 2 in., per cent	Reduction of area, per cent	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.‡	Elongation in 2 in., per cent	Reduction of area, per cent
1007	77,300	61,500	33.8	64.1	94,950	77,250	26.5	58.6
1008	78,000	66,850	32.8	74.6	96,900	88,650	28.8	68.5
1009	121,550	85,450	19.0	50.9	134,050	108,300	20.3	53.6
1010	88,650	50,600	28.5	56.1	106,850	89,700	25.0	55.3
1011	86,000	63,800	30.8	62.8	105,400	88,600	25.8	57.4
1012	80,000	62,000	32.0	62.3	100,050	84,050	25.5	56.8
1164	99,500	75,400	25.0	44.9	117,700	92,700	21.5	48.9
1165	71,600	54,000	36.0	68.9	76,900	62,400	33.0	66.9
1166	69,000	59,500	38.0	74.9	92,600	84,700	27.5	68.2
1167	96,100	86,200	28.0	66.2	108,600	101,500	25.0	64.1
1169								
1170								
1171	71,600	58,200	35.0	68.2	93,200	79,300	25.5	63.1

* Smith and Palmer.[368]

All steels forged perfectly except those containing tin and antimony, which were forgeable only with extreme care.

† Intended composition, not analysed. *Note:* Although in the original paper it is indicated that all of the values in the copper column were "intended compositions," it is probable that the values that contain two figures after the decimal point were determined by analysis.

Q. Silicon steels were quenched from temperatures stated.

‡ For an extension of 0.5 per cent.

§ Reannealed at 450°C. (840°F.) for 4 hr.

Note: In the original paper the yield strength for alloy 1165 was erroneously given as 84,000.

Data reported by Rädeker[369] for steels containing nickel, chromium, molybdenum, vanadium, cobalt, or titanium in addition to copper showed that these elements did not change the increase in strength brought about by the precipitation-hardening treatment.

Results recently obtained by Eilender, Fry, and Gottwald[390] show that manganese tends to suppress the precipitation-hardening effect of copper, at least when the manganese content is 2.5 per cent or more. Hardness-versus-reheating-temperature curves for water-quenched and for air-cooled alloys indicated that this resulted from precipitation of copper on cooling rather than from an increased solubility of copper in high-manganese alloys; precipitation hardening was more pronounced in the water-quenched than in the air-cooled samples.

C. INFLUENCE OF PRECIPITATION HARDENING ON PHYSICAL PROPERTIES

Some data on the change in electric resistance, density, and magnetic properties of copper steels during precipitation hardening have been obtained by Buchholtz and Köster.[257] These data are briefly reviewed below.

76. Electric Properties.—Figure 78 shows the properties of a copper-chromium steel hot rolled and then reheated to different

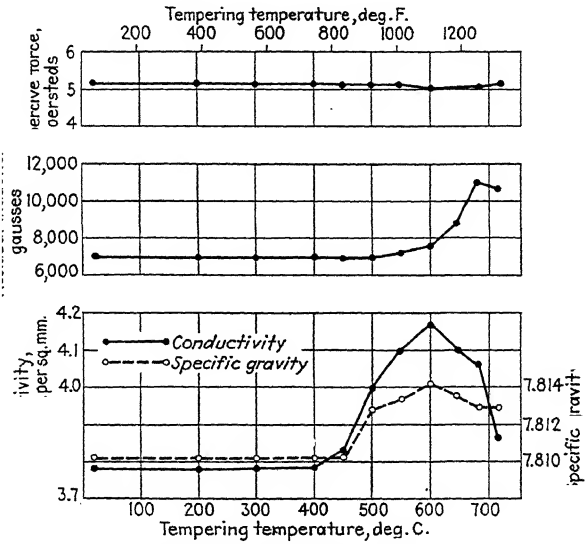


FIG. 78.—Influence of reheating temperature on the properties of a copper-chromium steel. (*Buchholtz and* .

temperatures for a period of 1 hr. The steel contained 0.15 per cent carbon, 0.41 per cent silicon, 0.93 per cent manganese, 0.024 per cent phosphorus, 0.029 per cent sulphur, 1.1 per cent copper, and 0.38 per cent chromium. Although the chromium undoubtedly influences the properties, it probably has little effect on the change in properties on reheating. The electric conductivity is increased by heating to temperatures within the range where precipitation takes place. This is the expected behavior, for precipitation produces a more dilute solution of copper in iron, and the more dilute the solution the greater should be the conductivity.

The conductivity of an alloy containing 0.04 per cent carbon and 5.0 per cent copper is shown in Fig. 79. The alloy in the hot-rolled condition was heated stepwise to higher and higher temperatures and air cooled from each temperature. The

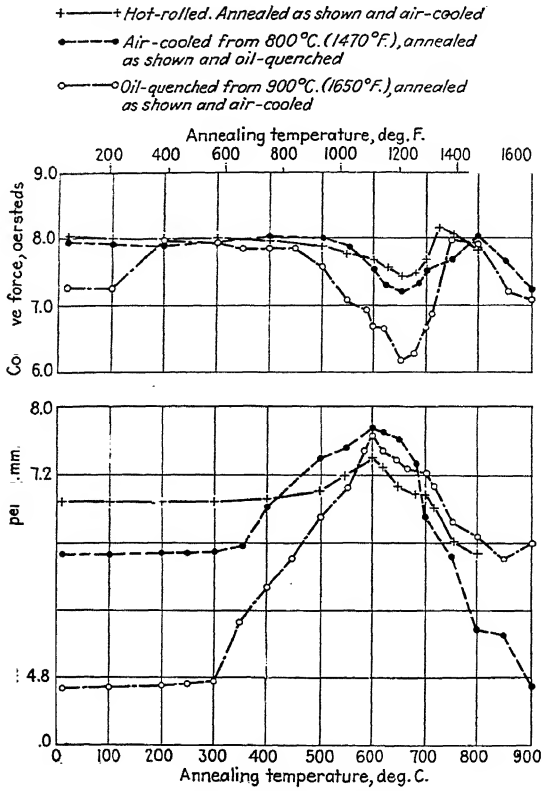


FIG. 79.—Influence of heat treatment on coercive force and electric conductivity of a 5 per cent copper alloy. (*Buchholtz and Köster.*[257])

conductivity increased to a maximum on heating to 600°C. (1110°F.) and then decreased. The specimen after air cooling from 800°C. (1470°F.) was then heated stepwise to different temperatures and quenched in oil from each temperature. After quenching in oil from 900°C. (1650°F.), the first series of treatments was repeated. The maximum amount of copper was in solution after quenching from 900°C. (1650°F.), and the

conductivity was, therefore, the lowest after this treatment. Copper apparently began to precipitate from the oil-quenched material on reheating to 350°C. (660°F.), for the conductivity began to increase at this temperature.

Figure 80 shows how the conductivity increases with time on holding a quenched 5 per cent copper alloy at temperatures of 500, 550, 600, and 650°C. (930, 1020, 1110, and 1200°F.).

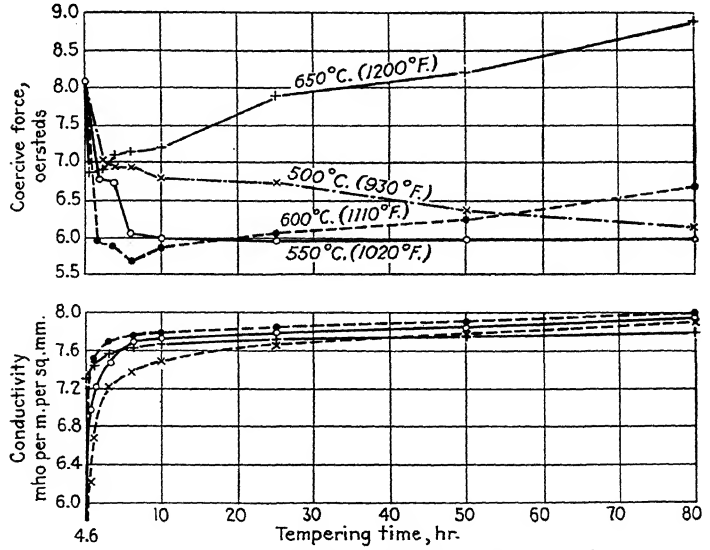


FIG. 80.—Change in coercive force and electric conductivity of a 5 per cent copper alloy, quenched from 900°C. (1650°F.) and held at the indicated temperatures. (*Buchholtz and Köster.*[257])

77. Magnetic Properties.—The values in Fig. 78 indicate that coercive force remains practically unchanged when precipitation hardening takes place in a 1 per cent copper alloy. Residual induction, however, increases as the copper is precipitated.

Figures 79 and 80 show that the coercive force of a 5 per cent copper alloy is influenced by precipitation of the copper. As compared with some other ferrous alloys, as iron-molybdenum or iron-tungsten, the influence of precipitation hardening on coercive force is quite small.

78. Density.—The data shown in Fig. 78 indicate that the specific weight of iron-copper alloys increases as the copper is precipitated from solution.

D. AUTHORS' SUMMARY

1. Iron-rich alloys containing more than 0.6 or 0.7 per cent copper can be hardened by precipitation.

2. The alloys need not be drastically quenched in order to produce a supersaturated solid solution of copper in iron which will respond to a precipitation-hardening treatment. In fact, air cooling of sections several inches in diameter suffices to keep the copper in solution. In order to obtain the full benefit of precipitation hardening, it is, therefore, necessary only to reheat air-cooled material to the precipitation temperature.

3. The maximum hardening effect is produced by reheating at, or by interrupted cooling from, 450 or 500°C. (840 or 930°F.). From 2 to 4 hr. are required to produce the maximum hardness increase at the higher temperature and approximately 10 hr. at the lower temperature. Hardening does not occur at temperatures below 400°C. (750°F.), at least for a time at temperature not exceeding 100 hr. At temperatures above 500°C. (930°F.) precipitation hardening occurs very rapidly, but the maximum hardness produced is not so great as that obtained at lower temperatures. A practical treatment is to reheat for 4 hr. at 500°C. (930°F.).

4. As the copper content is increased from 0.7 per cent, the hardening on reheating increases until the copper content is between 1 and 1.5 per cent. On further increase in copper content the hardening effect decreases. This is an unexpected behavior and should be given more consideration.

5. In steels containing 0.55 per cent or less carbon, and possibly in steels of higher carbon content, precipitation hardening increases the tensile strength and yield strength by 20,000 lb. per sq. in. The increase in strength is accompanied by some loss in ductility as gaged by elongation and reduction of area, but the material is not rendered notably brittle. Precipitation hardening also decreases the notched-bar impact resistance.

6. The addition of small amounts of other alloying elements to copper steels has little influence on their response to a precipitation-hardening treatment.

7. When copper precipitates from a supersaturated solid solution the electric conductivity, density, and residual induction increase. Coercive force is but slightly affected by precipitation.

CHAPTER VII

MECHANICAL PROPERTIES OF IRON-COPPER ALLOYS, COPPER-BEARING WROUGHT IRON, AND CAST STEEL

Iron-copper Alloys—Copper-bearing Wrought Iron—Copper in Plain and Alloy Cast Steels—Authors' Summary

From the results of the work on precipitation hardening reported in the previous chapter it is probable that iron-copper alloys, relatively free from carbon, should also respond to this treatment. The few available reports on such alloys, discussed in this chapter, indicate that this is the case. The effect of copper on the mechanical properties of wrought iron is also summarized in the present chapter, as are the few published (and several unpublished) investigations on the plain and alloy cast steels to which copper has been added.

A. IRON-COPPER ALLOYS

To date, commercially pure iron to which copper has been added as an alloying element has apparently found little commercial application. All of the four investigations which are summarized in this section were made on materials melted on a laboratory scale.

79. Tensile Properties of Iron-copper Alloys.—Burgess and Aston[53] determined the tensile properties of the series of iron-rich alloys described previously (page 76). The properties of the as-forged alloys are shown in Fig. 81 and those of the alloys annealed at 900°C. (1650°F.) in Fig. 82. The specimens had a diameter between 0.3 and 0.4 in. The figures also show scleroscope-hardness values of the same alloys, reported by Roush.[59] As is to be expected, the strength of the alloys increased with the copper content. The breaks in the curves for the annealed alloys are difficult to explain, because those for tensile strength and yield strength do not occur at the same copper content as those for elongation and reduction of area.

Burgess and Aston called attention to the marked difference between the tensile properties of the unannealed and the annealed

samples. They suggested some intermediate treatment not so drastic as the annealing treatment used in their experiment. Curves obtained by Lorig and MacLaren for fully annealed copper steels were similar to those given in Fig. 82.

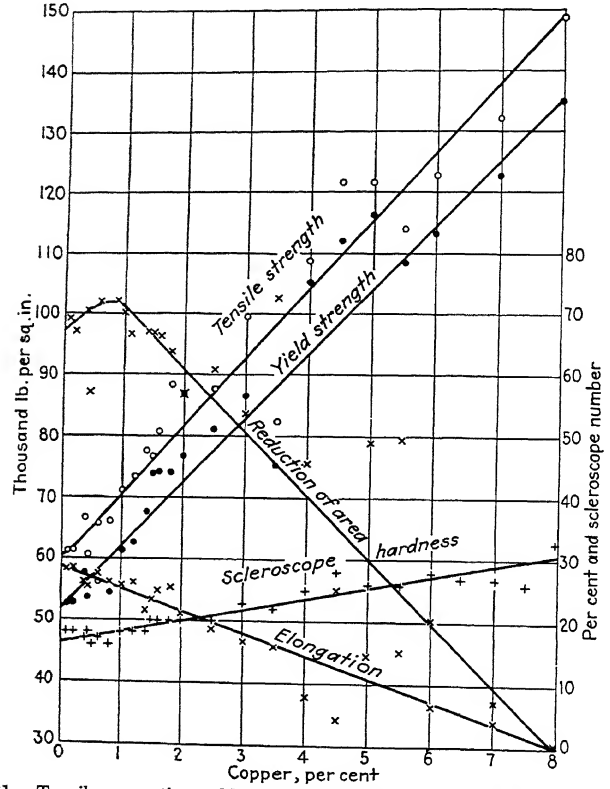


FIG. 81.—Tensile properties and hardness of forged iron-copper alloys. (*Burgess and Aston*[63] and *Roush.*[69])

80. Hardness of Iron-copper Alloys.—Scleroscope-hardness values of alloys containing 3, 5, 10, and 20 per cent copper, after quenching from different temperatures, were reported by Isihara[131] and are shown in Fig. 83. The alloys were made from Swedish iron and electrolytic copper in a Tammann furnace. There is an extraordinary agreement between the temperatures

of the breaks in the hardness curves and the temperatures of the transformations indicated by the iron-copper equilibrium diagram accepted at the time the work was done.

Rockwell-hardness values of vacuum-melted iron-copper alloys made from electrolytic iron and electrolytic copper by Kussmann and Scharnow[237,238] are shown in Fig. 84. The alloys were forged into rods, then annealed by heating at 800°C. (1470°F.), and cooled slowly. Within the range of solubility at either the copper-

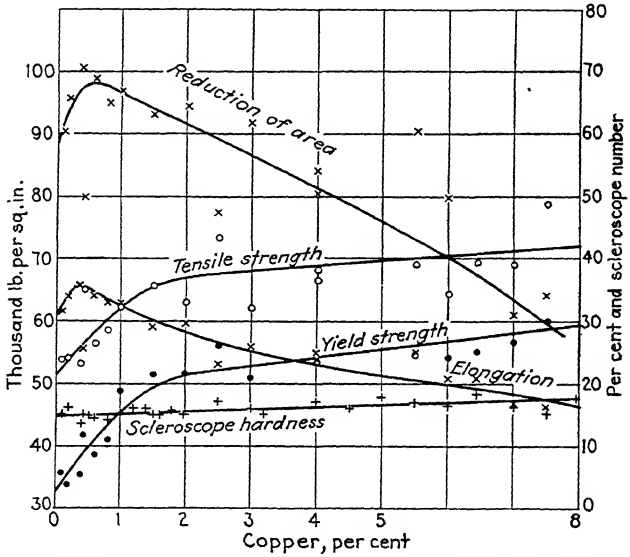


FIG. 82.—Tensile properties and hardness of annealed iron-copper alloys. (*Burgess and Aston*[53] and *Roush.*[59])

rich or the iron-rich end of the diagram the hardness increased rapidly as the solution became more concentrated. There is practically a straight-line relationship between hardness and composition in the heterogeneous field.

Rockwell-hardness values of Kussmann and Scharnow's[238] alloys containing up to 20.7 per cent copper and quenched in water from different temperatures are given in Table 31. The hardness of none of the alloys was greatly changed by quenching, and the results do not sharply indicate transition points as do those of Isihara.

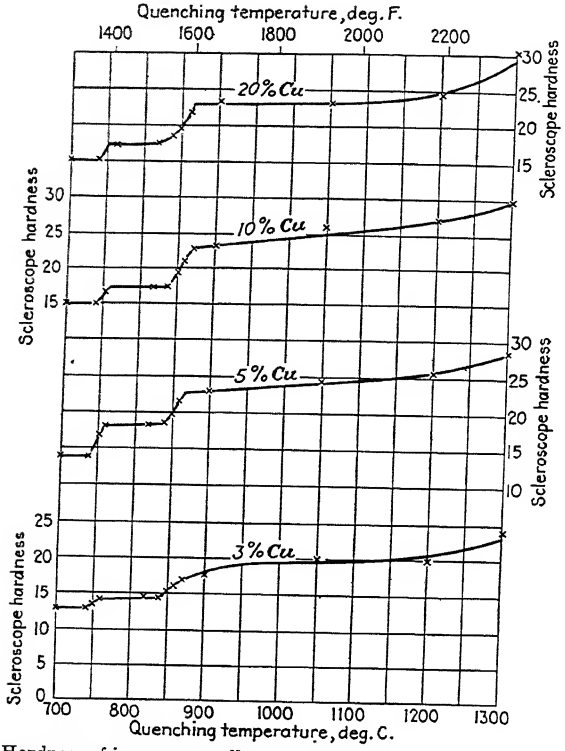


FIG. 83.—Hardness of iron-copper alloys, quenched from different temperatures. (*Isihara.*[131])

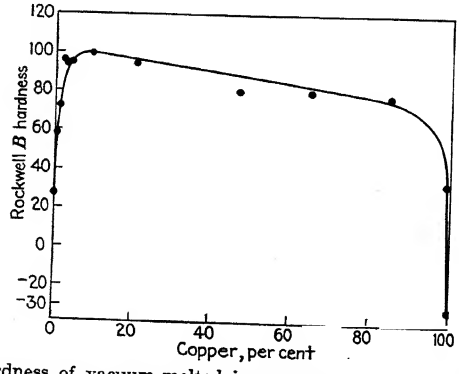


FIG. 84.—Hardness of vacuum-melted iron-copper alloys, annealed at 800°C. (1470°F.). (*Kussmann and Scharnow.*[237,238])

TABLE 31.—EFFECT OF QUENCHING ON HARDNESS OF IRON-COPPER ALLOYS*

Quenching temperature		Rockwell *B* Hardness							
		Copper, per cent							
°C.	°F.	0	0.5	1.0	2.4	2.7	4.0	9.0	20.7
Annealed		27	58	72	95	94	95	99	94
700	1290	28	..	..	..	92	94	98	93
740	1365	21	..	..	..	98	96	99	96
760	1400	38	..	..	..	98	96	101	96
800	1470	34	..	..	..	93	94	97	92
700	1290	36	58	70	94	89	90	94	92
800	1470	41	57	71	90	87	90	92	91
850	1560	34	59	72	93	90	91	95	91
920	1690	38	58	72	89	94	100	102	102
1020	1870	35	57	57	95	97	107	112	108

* Kussmann and Scharnow.[238]

B. COPPER-BEARING WROUGHT IRON

As will be discussed in Chapter IX, a number of investigators have been interested in the unusual corrosion resistance of some old wrought irons which were found to contain appreciable amounts of adventitious copper; some have attributed the long life to the presence of this element. The effect of copper on the strength properties of wrought iron has, however, aroused no interest since the turn of the century, and before that time the work was not comprehensive enough to permit any definite conclusions.

81. Mechanical Properties of Copper-bearing Wrought Iron.—Percy's[11] book published in 1864 reviews work reported on the influence of copper in iron, but the early work is hardly trustworthy. Mention is made of a patent by Longmaid (British patent 1863 of 1861) which claimed that if 2 lb. of copper were added to a ton of the iron used in the puddling process "the iron thus produced will be found to be possessed of a great degree of hardness whilst retaining its ductility." Percy was skeptical in regard to this great efficacy of copper.

In 1894, Arnold[24] reported that copper had a considerable hardening effect on wrought iron but that it did not produce brittleness.

Some actual tensile data of copper wrought irons were obtained in the eighteen-nineties by Lipin.[33] One of the irons contained

0.33 per cent copper and another 0.65 per cent copper. No difficulty was encountered in producing either iron. The results as given below indicate that there is little difference between the properties of the two materials, but by comparison with modern, copper-free wrought iron they may show a slight increase in strength and slight loss in ductility due to copper.

Iron	I	II
Carbon, per cent	0.08	0.09
Copper, per cent	0.33	0.65
Phosphorus, per cent	0.089	0.054
Tensile strength, lb. per sq. in.	53,600	56,600
Elongation, per cent	26.2	25.3
Reduction of area, per cent	44.3	40.9

C. COPPER IN PLAIN AND ALLOY CAST STEELS

Despite the fact that copper cast steels have been used commercially, data on the effect of copper on mechanical properties are few. The work of Nehl and Kinnear on copper in ordinary steel castings is summarized, and results are quoted from the unpublished investigations of Lorig and associates at Battelle Memorial Institute and Zuege of Sivyer Steel Casting Company, both of which tested material which should probably be classed as cast manganese-copper steel.

With the exception of the unpublished work of Finlayson on copper-bearing cast steels, most of which contained considerable manganese and silicon, the only data available on the effect of copper on cast alloy steels are those of Lorig and associates on copper-chromium steel and a few results of Kinnear. All of these will be discussed below.

82. Mechanical Properties of Cast Copper Steel.—Nehl[267] cast specimens from an electric-furnace heat, containing 0.16 per cent carbon, 0.55 per cent manganese, 0.43 per cent silicon, and 1.06 per cent copper. They were normalized at 900°C. (1650°F.), and some subsequently reheated to 500°C. (930°F.) for 2 hr. The properties after these treatments were:

Property	Normalized	Normalized and reheated
Tensile strength, lb. per sq. in.	74,600	88,200
Yield strength, lb. per sq. in.	50,800	65,400
Elongation, per cent	22.5	15.5
Reduction of area, per cent.	51.2	41.0
Impact resistance, m-kg.	12.0	9.0

The properties of this steel at elevated temperatures are given in Table 32, which also gives the properties of a carbon steel that had approximately the same strength at ordinary temperature. At all temperatures the normalized and reheated copper steel had a higher yield strength than the carbon steel. At temperatures of 400°C. (750°F.) and above the copper steel is not to be recommended, because it would tend to soften with time owing to agglomeration of the copper, but at lower temperatures its properties are effectively stable. Nehl compared the properties of the copper steel with properties of low-alloy cast steels reported by Rys[268] and showed that for slightly elevated temperatures (below 400°C. or 750°F.) the strength of the copper steel was as great as that of other low-alloy steels.

TABLE 32.—PROPERTIES OF CAST STEELS AT ELEVATED TEMPERATURES*

Material†	Testing temperature		Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, per cent	Reduction of area, per cent
	°C.	°F.				
A	20	70	74,600	50,800	22.5	51.2
B	20	70	88,400	65,400	15.0	41.0
C	20	70	86,800	49,100	17.6	27.6
A	100	210	68,700	47,800	22.1	46.4
B	100	210	81,400	61,600	13.9	42.7
C	100	210	80,400	41,300	18.5	30.5
A	200	390	68,000	45,100	17.3	39.5
B	200	390	82,700	58,900	13.0	36.0
C	200	390	80,300	36,700	16.3	28.0
A	300	570	67,200	36,300	15.3	31.0
B	300	570	80,500	50,800	14.6	24.4
C	300	570	85,100	34,900	20.3	22.0
A	400	750	60,800	34,200	18.0	20.5
B	400	750	66,100	43,500	15.6	23.7
C	400	750	71,600	30,900	25.3	46.9

* Nehl.[267]

† *A*—0.16 per cent carbon, 1.06 per cent copper, normalized.
B—Same steel, normalized and then reheated to 500°C. (930°F.).
C—0.38 per cent carbon (no copper), annealed at 930°C. (1705°F.).

Properties of normalized and normalized and reheated steels containing different amounts of copper and carbon, as determined

by Kinnear,[291] are listed in Table 33. The data for specimens 1 to 5 show that for steels containing 0.3 or 0.4 per cent carbon the strength of the normalized material increases as the copper content is increased to 5 per cent. Reheating the normalized steels results in precipitation hardening, the maximum increase in strength occurring with 1 per cent copper. The increase in tensile strength and yield strength of the 1 per cent copper steel (No. 3) brought about by precipitation hardening was approximately 15,000 lb. per sq. in. The increase in hardness was accompanied by a slight increase in ductility as indicated by elongation and reduction of area. In the low-carbon specimens, Nos. 6 and 7, precipitation hardening increased tensile strength and yield strength by approximately 20,000 lb. per sq. in. and decreased ductility.

TABLE 33.—PROPERTIES OF HEAT-TREATED CAST STEELS*

Steel	Composition, per cent			Condition†	Tensile strength, lb. per sq. in.	Yield strength,‡ lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell hardness
	C	Mn	Cu						
1	0.41	....	0.50	N	99,400	62,500	14.0	18.8	187
				R	101,200	64,400	18.0	26.4	196
2	0.32	....	0.76	N	90,800	58,250	15.5	23.3	174
				R	92,200	59,750	18.5	32.5	179
3	0.29	....	0.94	N	88,200	58,250	19.0	31.2	179
				R	103,900	75,700	20.5	36.4	207
4	0.31	....	2.72	N	105,200	87,500	11.0	18.5	217
				R	110,300	92,250	14.5	28.5	228
5	0.32	....	4.98	N	118,750	97,550	9.0	14.1	255
				R	118,500	99,000	11.5	22.3	248
6	0.09	0.64	0.96	N	70,650	45,250	31.0	59.8	143
				R	87,650	68,750	24.5	57.5	187
7	0.13	0.62	1.00	N	70,000	50,000	31.0	54.1	143
				R	89,000	69,750	23.5	49.7	196

* Kinnear [291]

† N—Normalized, steels 1 to 5 at 845°C. (1550°F.), steel 6 at 900°C. (1650°F.), and steel 7 to 870°C. (1600°F.).
R—Reheated after normalizing, steels 1 to 5 to 540°C. (1000°F.), steel 6 to 480°C. (900°F.), and steel 7 to 510°C. (950°F.).

‡ Reported as yield point.

... per cent carbon, 0.60 to 1.4 e, and about 0.50 per cent silicon. From 1.00 to 2.00 per cent copper was added. The exact compositions are given in Table 34.

TABLE 34.—COMPOSITION OF STEELS PREPARED BY LORIG AND ASSOCIATES

Heat	Casting	Composition, per cent					
		C	Si	Mn	Cu	S	P
A	1	0.20	0.33	0.76	....	0.032	0.017
	2	....	....	....	1.00		
	3	....	....	....	1.33		
B	4	0.49	0.44	1.48			
C	5	0.50	0.44	1.32			
	6	....	....	....	1.08		
	7	....	....	....	1.47		
D	8	0.60	0.42	1.25			
	9	....	....	....	1.08		
	10	....	....	....	1.52		
E	11	0.27	0.47	1.03	1.13		
F	12	0.22	0.46	0.94	1.19	0.035	0.018
G	13	0.16	0.45	0.92			
	14	....	....	....	1.04		
	15	....	....	....	1.46		
H	16	0.16	0.40	0.90			
	17	....	....	....	1.15		
I	18	0.25	0.43	0.93			
J	19	0.39	0.52	0.95			
	20	....	....	....	1.22		
	21	....	....	....	1.63		
K	22	0.40	0.42	0.91	1.24		
L	23	0.37	0.43	0.93	1.20		
M	24	0.15	....	0.60			
	25	....	....	....	1.16		
	26	....	....	....	1.66		
N	27	0.19	....	0.63			
	28	....	....	....	1.27		
	29	....	....	....	1.88		

These steels were melted in a magnesia crucible of 50-lb. capacity in a high-frequency furnace, and bars approximately

* Unpublished work done by C. H. Lorig, D. E. Krause, and G. L. Craig at Battelle Memorial Institute.

1 in. in diameter and 6 in. long were cast into molds of baked core sand. Many of the bars were unsound, which may be attributed to the fact that they were poured from the top instead of from the bottom. Tensile properties and hardness values of the bars in

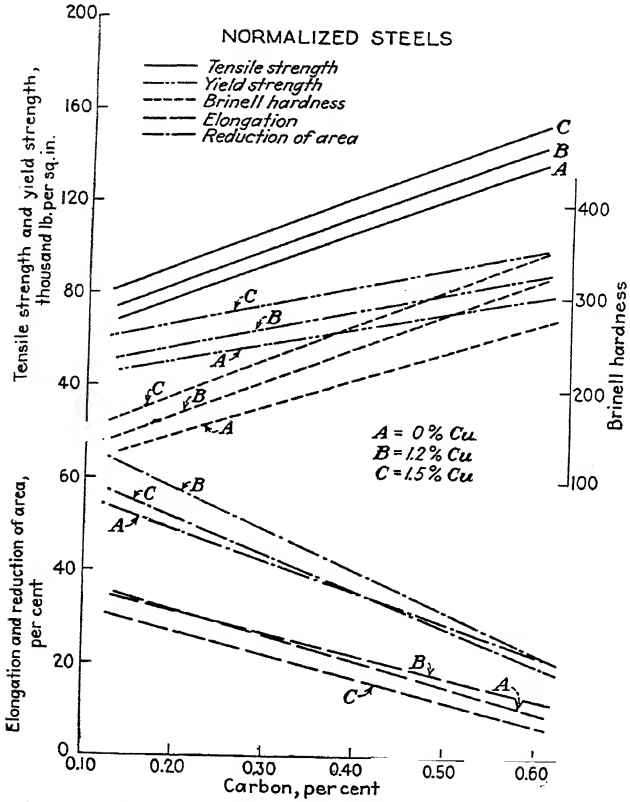


FIG. 85.—Mechanical properties of normalized cast steels, held at 900°C. (1650°F.) for 5 hr., air cooled, reheated to 855°C. (1575°F.), held 1 hr., and air cooled. (*Lorig and associates.*)

several conditions are shown in Figs. 85 to 88. The curves in these figures show that in normalized, in normalized and tempered, in precipitation-hardened, and in fully annealed steels 1.2 or 1.5 per cent copper increases hardness and strength and decreases ductility as determined by the tensile test. The difference in strength between the copper steels and the unalloyed

steels was greatest when the samples had been given a heat treatment which would produce precipitation hardening.

Zuege* compared the properties of cast steels containing about 0.30 per cent carbon and 0.73 and 1.26 per cent manganese with

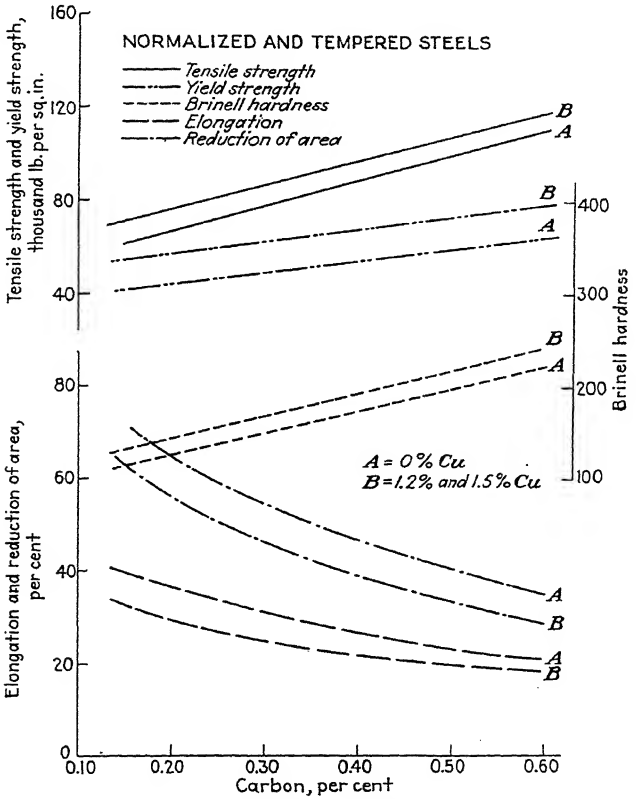


FIG. 86.—Mechanical properties of normalized and tempered cast steels. Normalized as described for Fig. 85 and then tempered for 2 hr. at 675°C. (1250°F.). (*Lorig and associates.*)

and without the addition of 0.97 and 1.92 per cent copper. One series was given an arrested cooling, holding at 540°C. (1000°F.), while another was normalized and reheated at 540°C. (1000°F.), both with the aim of bringing about some precipitation hardening.

These steels had normal silicon content and higher carbon content than those of Finlayson (see page 183). With the excep-

* Private communication.

tion of heat 297-5 and 6 compared with 297-7 and 8, the increased yield strength due to copper is obtained at the expense of some decrease in ductility. The data appear in Table 35.

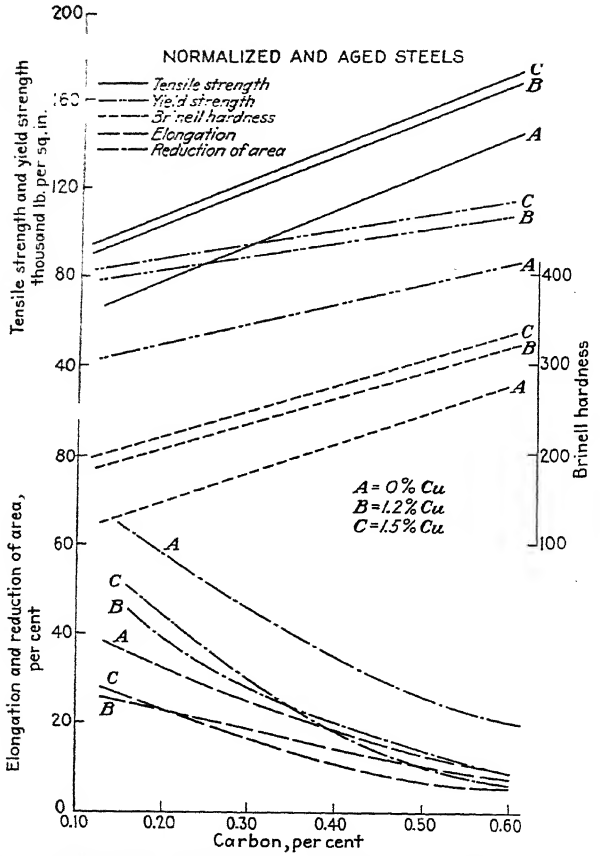


FIG. 87.—Mechanical properties of normalized and "aged" cast steels. Normalized as described for Fig. 85 and then heated for 3 hr. at 500°C. (930°F.). (*Lorig and associates.*)

84. Mechanical Properties of Cast Copper Steels Containing Other Alloys.—The properties of four cast steels containing about 1 per cent copper and a small amount of molybdenum, vanadium, chromium, or zirconium, as determined by Kinnear,[291] are shown

in Table 36. All of these responded to the precipitation-hardening treatment.

Lorig and associates tested some cast copper-chromium steels made in the same manner as the steels mentioned previously.

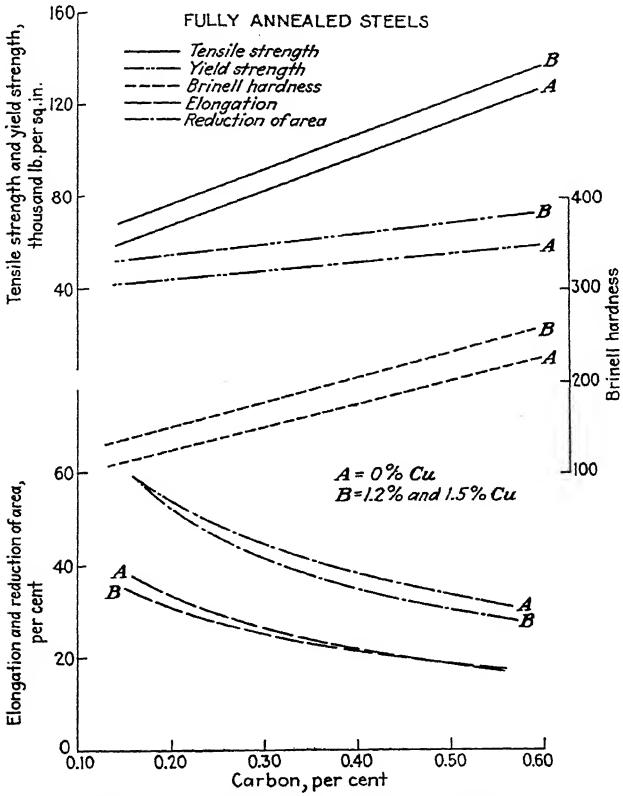


FIG. 88.—Mechanical properties of fully annealed cast steels. Held at 900°C. (1650°F.) for 5 hr., air cooled, reheated to 855°C. (1575°F.) for 1 hr., and furnace cooled. (*Lorig and associates.*)

Their results are given in Table 37, but they are hardly adequate to show whether the steels compare favorably with other low-alloy steels.

85. Mechanical Properties of Cast Silicon-manganese-copper Steels.—In a private communication A. Finlayson* of Pacific Car and Foundry Company supplied some data and comments

* Apr. 16, 1934.

TABLE 35.—PROPERTIES OF CAST STEELS*

Heat number	Bar number	Composition, per cent						Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell hardness	Al per ton†	Heat treatment
		C	Mn	Si	P	S	Cu							
296–1 and 2	Com 6	0.27	0.73	0.34	0.027	0.032	....	78,200 77,900	46,400 46,000	27.0 27.5	41.0 42.9	170 170	10 oz.	*A*
296–3 and 4	Cu 2	0.26	0.73	0.34	0.027	0.032	0.97	89,800 89,200	57,800 57,500	22.0 23.0	40.3 41.6	197 187 197	10 oz.	*A*
297–5 and 6	Nuloy 1	0.32	1.26	0.46	0.034	0.038	....	94,900 90,200	54,600 56,900	23.0 22.0	35.7 33.5	201 197 201	6 oz.	*A*
297–7 and 8	Cu 3	0.32	1.26	0.46	0.034	0.038	1.92	103,900 103,400	69,100 68,200	22.0 21.5	34.7 37.2	217 217 229	6 oz.	*A*
296–9	Com 8	0.27	0.73	0.34	0.027	0.032	....	85,300	55,900	25.0	44.0	187	.....	*B*
296–10	Cu 4	0.27	0.73	0.34	0.027	0.032	0.97	106,300	76,300	21.5	43.7	229	.....	*B*
297–11	Nuloy 7	0.32	1.26	0.46	0.034	0.038	....	103,700	67,700	24.0	51.4	229	.....	*B*
297–12	Cu 9	0.32	1.26	0.46	0.034	0.038	1.92	137,300	104,900	16.0	39.0	285	.....	*B*
297–13	Nuloy	0.32	1.26	0.46	0.034	0.038	....	91,900	53,400	27.5	57.1	197	.....	*C*

* Zuege, Sivyer Steel Casting Company.

† Aluminum added in the bull ladle.

Heat treatment: *A*: Heated to 900°C. (1650°F.), furnace cooled to 540°C. (1000°F.), and held 4 hr. *B*:Heated to 900°C. (1650°F.), air quenched, and reheated to 540°C. (1000°F.). *C*: Heated to 900°C. (1650°F.), air quenched, and tempered at 690°C. (1275°F.).

TABLE 36.—PROPERTIES OF HEAT-TREATED CAST STEELS CONTAINING COPPER AND ONE OTHER ELEMENT*

Number	Composition, per cent				Condition†	Tensile strength, lb. per sq. in.	Yield strength,‡ lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell hardness
	C	Mn	Cu	Other element						
1	0.26	0.73	0.88	0.36 Mo	N	101,900	59,800	17.5	24.4	196
					R	104,000	79,000	22.0	41.0	217
2	0.29	0.72	0.89	0.20 V	N	99,800	69,500	18.0	30.5	192
					R	106,750	81,700	21.5	43.7	212
3	0.35	0.73	1.02	0.63 Cr	N	107,500	70,750	17.5	27.5	207
					R	122,000	88,350	17.5	30.2	228
4	0.32	0.70	1.04	0 22 Zr	N	101,000	68,250	16.5	21.3	187
					R	115,300	87,400	13.0	16.3	228

* Kinnear.[291]

† N—Normalized at 845°C. (1550°F.).
R—Reheated to 540°C. (1000°F.) after normalizing.

‡ Reported as yield point.

on copper-bearing cast steels made in regular production. Experiment and experience with steels containing 0.5 to 4.0 per cent copper have convinced Finlayson that the addition of this element to commercial materials does not result in greater improvement of properties than may be obtained by increasing or adjusting the amounts of carbon, silicon, and manganese.

Finlayson believes that castings should be annealed rather than normalized; the treatment consists of heating to 900°C. (1650°F.) for 3 to 5 hr., depending upon the cross-section, and cooling to ordinary temperature in 4 hr. or less. This is the treatment given steels 1, 2*A*, 5, 6, and 7 in Table 38. The steels thus annealed may be hardened by reheating to 525°C. (975°F.) as shown by specimens 1 and 1*A*. For the type of copper steel used, this annealing treatment gives better results than normalizing as is shown by specimens 2 and 2*A*.

Finlayson believes that when copper is added to a cast steel the carbon content must be lowered if optimum ductility for a given yield strength is to be obtained. If the carbon is lowered, the silicon or manganese or both may be raised. This is shown by steels 3 and 4 which were annealed 3 hr. at 950°C. (1740°F.) and furnace cooled. The softer steel, owing to the use of copper, has a higher yield strength without loss of ductility.

TABLE 37.—PROPERTIES OF CAST COPPER-CHROMIUM STEELS*

Composition, per cent			Heat treatment†	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in. per cent	Reduction of area, per cent	Brinell hardness
C	Cu	Cr						
0.32	....	0.50	6	102,500	77,750	19.0	48.1	212
0.32	0.96	0.50	4	92,000	60,250	24.5	43.4	170
0.32	0.96	0.50	5	111,000	95,500	20.5	56.8	229
0.32	1.78	0.50	2	96,250	64,750	25.5	55.5	187
0.32	1.78	0.50	5	116,250	102,750	19.5	55.2	248
0.28		1.01	2	90,750	57,500	26.0	47.8	174
0.28		1.01	4	88,000	50,500	24.5	39.8	167
0.28		1.01	3	133,000	95,500	11.0	15.2	262
0.28	.99	1.01	4	96,000	60,500	24.5	44.3	179
0.28	.99	1.01	6	115,250	99,000	18.0	44.9	235
0.28	.85	1.01	1	149,500	125,000	4.0	7.0	302
0.28	85	1.01	3	147,500	127,500	8.5	12.2	302
0.28	85	1.01	5	118,500	105,000	18.0	46.3	235
0.28		1.01	6	119,500	105,000	15.0	33.8	248
0.30		1.81	1	161,500	150,000	3.0	4.7	341
0.30		1.81	3	154,500	128,700	9.0	11.5	311
0.30		1.81	2	107,200	83,500	19.0	44.9	212
0.30		1.81	5	119,000	99,250	20.0	56.2	235
0.30	0.96	1.81	1	160,000	150,000	2.5	3.1	341
0.30	0.96	1.81	6	121,250	103,000	16.5	37.3	248
0.30	1.84	1.81	3	173,000	145,000	7.0	10.8	352
0.30	1.84	1.81	5	120,000	100,000	19.5	48.9	262

*Lorig and associates.

† 1. Normalized at 900°C. (1650°F.) for 5 hr.; 855°C. (1575°F.) for 1 hr.

2. Normalized as in 1. Tempered at 675°C. (1250°F.) for 2 hr.

3. Normalized as in 1. Reheated to 500°C. (930°F.) for 3 hr.

4. Normalized at 900°C. (1650°F.) for 5 hr. Annealed at 855°C. (1575°F.) for 1 hr.

5. Normalized at 900°C. (1650°F.) for 5 hr. Water quenched from 855°C. (1575°F.). Tempered at 675°C. (1250°F.) for 2 hr.

6. Normalized at 900°C. (1650°F.) for 5 hr. Oil quenched from 855°C. (1575°F.). Tempered at 675°C. (1250°F.) for 2 hr.

Steel 5 is cited by Finlayson as another annealed silicon-manganese-copper steel with excellent properties, and specimens 6 and 7 show that annealed steels of high silicon and manganese percentages together with higher carbon content may have satisfactory ductility. The yield strength, however, of the lower carbon specimen (No. 6) is much higher than that of the other (No. 7).

TABLE 38.—COMPOSITION AND MECHANICAL PROPERTIES OF SILICON-MANGANESE-COPPER STEELS TESTED BY FINLAYSON

Steel number	Composition, per cent					
	C	Mn	S	P	Si	Cu
1	0.14	1.58	0.016	0.023	1.08	1.83
2	0.23	1.31	0.025	0.022	0.89	1.83
3	0.28	1.06	0.014	0.018	0.33	none
4	0.08	1.06	0.020	0.022	0.72	1.25
5	0.14	1.25	0.018	0.023	1.28	1.80
6	0.20	1.16	0.030	0.023	0.70	1.75
7	0.27	1.27	0.026	0.052	0.30	1.72
8	0.11	1.04	0.024	0.035	1.23	1.74

Steel number	Treatment	Properties				
		Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Sclerescope hardness
1	Annealed	90,000	68,000	26.55	51.35	26
1*A*	Annealed and reheated to 525°C. (975°F.)	92,000	77,500	29.65	57.00	25
2	Normalized	95,500	71,500	18.7	26.4	30
2*A*	Annealed	98,500	80,000	23.4	37.2	29
3	Annealed at 950°C. (1740°F.)	82,500	48,200	31.2	46.0	154*
4	Annealed at 950°C. (1740°F.)	74,600	56,300	31.2	61.0	138*
5	Annealed	90,000	72,500	29.6	52.7	
6	Annealed	93,500	80,000	23.4	41.5	
7	Annealed	89,500	61,700	25.0	40.0	
8	Annealed at 950°C. (1740°F.)	81,400	64,100	31.25	55.95	23
8*A*	Annealed as above, normalized at 860°C. (1580°F.), and tempered at 490°C. (915°F.)	106,750	88,500	25.00	53.30	39

* Brinell hardness.

In reference to precipitation hardening Finlayson wrote:

Concerning the phenomenon of precipitation hardening, I have found that the properties obtainable in the laboratory are easily reproduced in

a commercial way with large heat-treating charges of as much as 20 tons. For the most part I have obtained results very similar to those of Kinnear, although I am not wholly in agreement with the statement that the maximum increase in strength occurs with 1 per cent copper. This may hold for the normalized high-carbon steels shown in Table 33 (see page 174) but even here there is too great a spread in copper content between steels 3 and 4 to render such conclusive. Actually, I have developed higher properties with considerably more than 1 per cent copper, although with a somewhat different heat treatment and with a modified composition. In specimens No. 8 and 8A* I show the effect of precipitation hardening on such a steel which was first annealed at 950°C. (1740°F.) for 3.5 hr., then normalized at 860°C. (1580°F.), and tempered at 490°C. (915°F.). This is a typical heat and a treatment which we commonly use to develop the best properties in commercial castings. It will be noted that we have here obtained an increase in both yield strength and tensile strength of more than 24,000 lb. per sq. in.

The properties of some typical heats of copper steels of the type marketed under the trade name "Carcometal" are shown in Table 39. All of the properties are for annealed castings, although the annealing was not always in accordance with the moderately rapid cooling mentioned above.

Describing these Finlayson wrote:

Each heat given in this list represents the typical, or average properties of dozens of almost identical compositions, deliberately repeated in order to establish the degree of consistency to be expected in commercial practice. These heats are not laboratory, or experimental tests, but represent actual commercial castings produced in a basic electric furnace in melts of from 3 to 5 tons each. In the past few years we have manufactured several hundred tons of this material which has been used not only successfully, but with marked advantages in almost every industrial application, from heavy locomotive castings to case-hardened gears. In this latter application it has replaced many forgings as it has also in shafting, which we have cast up to 17 ft. long and 15 in. in diameter. We have also made many steam shovel sticks in box sections, and single piece booms up to 28 ft. long, all cast from one end through a single gate.

Further comments made by Finlayson are that in the cast copper steels, as made and treated by him, the proportional limit is seldom less than 95 per cent of the yield strength, the

* In this class of steels, Finlayson prefers to hold the carbon below 0.12 per cent.

low-carbon copper steels may be successfully case hardened, the fluidity of the copper steel adapts it to the pouring of unusually long, thin sections, and a denser and more fluid weld than with carbon steels may be obtained in both electric and oxy-acetylene welding.

TABLE 39.—PROPERTIES OF COMMERCIALLY PRODUCED ANNEALED MANGANESE-SILICON-COPPER STEEL CASTINGS*

Composition, per cent				Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent
C	Mn	Si	Cu				
0.08	1.06	0.72	1.24	74,600	56,300	31.2	61.0
0.09	1.22	0.94	1.86	74,200	59,300	31.2	58.3
0.09	1.10	0.72	1.14	75,000	56,000	35.9	67.0
0.10	1.19	0.84	1.27	79,500	56,000	34.3	58.5
0.11	0.99	0.37	1.52	78,000	59,500	29.6	51.9
0.11	0.84	0.21	1.57	80,000	58,000	29.6	49.4
0.12	1.15	0.96	2.13	83,700	64,400	34.3	58.0
0.12	1.05	0.91	1.67	79,500	56,000	34.3	58.5
0.12	1.72	1.24	2.02	82,700	65,700	34.3	60.3
0.12	0.98	0.88	1.87	78,700	58,700	34.3	58.8
0.12	1.07	1.03	2.22	79,300	62,200	31.2	55.7
0.13	1.28	0.63	2.24	75,150	53,200	32.8	64.0
0.13	0.87	0.62	1.65	75,000	51,500	31.2	57.2
0.13	1.13	0.77	1.89	78,000	57,000	29.6	56.7
0.14	1.46	0.96	2.11	85,000	65,000	31.2	53.3
0.15	1.28	1.11	1.97	85,800	64,000	28.1	44.8
0.15	1.08	1.09	1.89	89,700	69,500	29.7	57.0
0.16	0.89	1.18	1.70	83,800	62,200	31.2	50.5
0.16	1.12	0.86	2.20	81,500	59,000	31.2	55.4
0.16	1.38	1.34	1.77	91,000	69,000	28.1	54.1
0.17	1.02	0.77	1.77	80,200	58,000	29.6	50.8
0.17	1.18	1.12	1.80	82,200	61,500	31.2	54.9
0.18	1.14	1.16	2.39	83,500	65,300	31.2	53.8
0.18	0.82	1.40	2.40	85,800	65,700	29.6	47.7
0.19	1.35	1.04	2.17	86,200	63,500	31.2	56.5
0.19	1.25	1.17	2.03	81,800	60,300	29.6	57.3
0.20	1.16	0.70	1.75	93,500	80,000	23.4	41.5
0.23	1.11	1.58	1.51	92,200	69,200	29.6	44.2
0.27	1.27	0.30	1.72	89,500	61,700	25.0	40.0
0.28	1.44	1.29	1.89	104,500	72,750	17.1	20.5

* Finlayson.

An approximate comparison between a cast silicon-manganese steel without added copper and one with high copper may be

drawn by bringing together the data for a steel tested by Schulz and Bonsmann, as summarized in Table 74 (page 265) of "The Alloys of Iron and Silicon" and those on one of Finlayson's steels, as follows:

Steel	Composition, per cent				Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent
	C	Mn	Si	Cu				
*A**	0.17	1.11			71,000	51,000	26†	54
B‡	0.17	1.18	1.12	1.80	82,200	61,500	31	55

* Schulz and Bonsmann—Steel *F*, annealed for 0.5 hr. at 980°C. (1795°F.), furnace cooled.
† Gage length not given.
‡ Finlayson, from Table 39. Annealed by Finlayson's procedure.

D. AUTHORS' SUMMARY

1. Copper added to low-carbon irons such as ingot iron increases tensile and yield strength. In the as-wrought condition the increase is continuous at least up to approximately 7 per cent copper, while the ductility is but slightly affected up to 1 per cent copper, above which it falls. The properties of the alloys with 1 per cent or more copper can be altered by heat treatment.

2. In the annealed condition tensile and yield strength increase rapidly up to some 2 per cent copper, beyond which they increase more slowly. Ductility increases slightly to about 0.5 per cent copper and then falls slowly. More data are needed on the properties of this class of alloys.

3. Data on copper in wrought iron are scarce. What few are available probably indicate a similar effect to that shown in ingot iron.

4. Copper exerts a definite alloying effect in cast steel, materially raising tensile and yield strength. Opinion on the optimum amount of copper varies, the suggested low limit being about 1 per cent, the high limit 2 per cent.

5. As is the case with the introduction of most alloying elements in steel, it is probably advisable, when ductility is a prime object, to reduce the carbon slightly when a material amount of copper is added. With such adjustment of composition, the effect of copper in an annealed or normalized cast steel is to improve tensile and yield strength with little or no loss in ductility.

6. By cooling at a rate adequate to hold copper in solid solution—this cooling rate may be quite slow—and then either arresting the cooling and holding the steel at the precipitation-hardening temperature, around 480 to 540°C. (900 to 1000°F.), or reheating and holding in that temperature range after cooling below it, a further increase in tensile and yield strengths may be obtained. In the higher carbon steels the ductility suffers somewhat as a result of this treatment.

7. A treatment which brings about only partial precipitation hardening, but superimposes some of the effects of precipitation hardening upon those ascribable to the straight alloying effect, may have possibilities.

8. The precipitation-hardening effect is obtained in the presence of various other alloying elements. It is most beneficial, if both strength and ductility are considered, when neither the carbon nor the other alloying elements are in excessive amounts, *i.e.*, when the steel is not too hard to start with. With composition so "balanced" as to utilize properly the effect of copper, the desirable properties of many alloy cast steels should be enhanced by the use of copper.

9. Using somewhat different types of steel both Kinnear and Finlayson demonstrated in large-scale commercial production that copper steels are readily handled in the foundry, and that the copper steel castings have performed well in service.

10. Copper deserves to be added to the list of useful alloying elements for cast steel.

CHAPTER VIII

MECHANICAL PROPERTIES OF WROUGHT COPPER STEELS

Properties at Ordinary Temperature—Properties at Elevated Temperatures—Special Properties—Authors' Summary

Copper steels may be divided into two classes: (1) those with from 0.2 to 0.5 per cent copper, and (2) those containing more than 0.5 per cent copper. The steels of class 1 are used chiefly for the manufacture of materials resistant to atmospheric corrosion and are generally referred to as "copper-bearing steels." The mechanical properties of the low- and medium-carbon steels are not appreciably affected by 0.5 per cent copper, and those steels to which copper is added to improve the mechanical properties belong to class 2. A large tonnage of steels of class 1 is used, but a comparatively small quantity of steels containing over 0.5 per cent copper has been made in this country, although complex low-alloy steels containing from 0.5 to 1 per cent copper have recently been marketed abroad. The most familiar of these materials is the copper-chromium steel whose properties are described in Chapter XI.

A. PROPERTIES AT ORDINARY TEMPERATURE

As was pointed out in Chapter VI, steels containing over 0.7 per cent copper can be hardened by precipitation of copper, and even normalized steels harden by precipitation when reheated to 500°C. (930°F.). The precipitation hardening of copper steels was not recognized until a few years ago, and in the early work on copper steels the materials were not treated to take advantage of this phenomenon.

86. Early Work.—In 1889, Ball and Wingham[17] stated that information available regarding the influence of copper on the properties of iron and steel was obtained on samples of uncertain composition and "before the necessity of submitting metals to rigorous mechanical tests was well understood." A few data on the strength of specimens of low-carbon copper steels cut from small ingots were reported, but they are of little interest now. A surprising finding was that a forged alloy "free from carbon"

and containing 4.44 per cent copper was so hard that it could scarcely be cut by a hack-saw.

In 1895, Lipin[33] reported the results of a comprehensive study of the influence of copper on the properties of steel. He prepared three series of alloys containing 0.1, 0.5, and 1.0 per cent carbon respectively. The copper content of the forged samples was as high as 4.75 per cent. Samples were tested as forged, as normalized, and after quenching in either oil or water. He found that for each of the series and for each heat treatment copper increased the strength and decreased the ductility as indicated by tensile tests. Tensile strength, elongation, and reduction of area were reported for each steel, but yield strength was reported for only a few samples. Although Lipin's data are probably accurate and give some information regarding the properties of many copper steels, they are omitted because they would add little to the knowledge obtainable from recent data on steels which had received more appropriate heat treatments.

Campbell,[26] in his book published in 1896, gave evidence to show that the presence of 0.25 per cent copper in low-carbon steels had no effect on the mechanical properties except to raise slightly the yield strength. Campbell's data on the influence of a small amount of copper on the properties of hot-rolled angles are given in Table 40. In commenting on these results Campbell said:

> It will be noted that no difference is to be found in the tensile strength between steels with high and low copper, although all the heats were made in the same way as nearly as possible, the workmen not knowing either in the Bessemer department or in the rolling mill what kind of iron was in use. Moreover, the high copper gives a slightly higher elastic ratio, which is a benefit, and also a better elongation and reduction of area.

TABLE 40.—PROPERTIES OF LOW-COPPER AND HIGH-COPPER STEEL ANGLES*

Thickness, in.	Copper, per cent	Number of heats	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 8 in., per cent	Reduction of area, per cent	Elastic ratio
5/16	0.10	11	61,400	44,200	27.5	56.3	71.9
5/16	0.35	17	60,300	43,800	27.9	59.0	72.7
3/8	0.10	10	59,000	42,200	28.85	55.5	71.6
3/8	0.35	11	59,600	43,500	29.0	57.9	72.9

* Campbell.[26]

In determining the influence of copper on the properties of rail steels Stead and Evans,[38] in 1901, made four split heats* of Bessemer rail steel and one split heat of open-hearth plate steel. The rail steels contained less carbon than is found in present-day rails; they contained from 0.3 to 0.5 per cent carbon and as much as 2 per cent copper. The plate steel contained 0.31 per cent carbon, and one-half of the heat contained 0.46 per cent copper. Drop tests and tensile tests indicated that as much as 2 per cent copper slightly increased the tensile strength and yield strength of the rails. It might be noted here, however, that the rails with 2 per cent copper cracked in the flanges during rolling; all other rails rolled satisfactorily. The results of the tensile tests and drop tests on rails from one heat were:

Property	Without copper	With copper
Carbon, per cent	0.48	0.49
Copper, per cent	0.03	0.89
Tensile strength, lb. per sq. in.	107,500	110,800
Yield strength, lb. per sq. in.	55,500	60,700
Elongation in 2 in., per cent	21.0	23.0
Reduction of area, per cent	32.0	37.0
Deflection after first blow, in.	3.375 to 3.5	3.125 to 3.25
Deflection after second blow, in.	6.125 to 6.375	5.75 to 6.0625

Results of tensile tests on the plates were:

Property	Without copper	With copper
Carbon, per cent	0.32	0.31
Copper, per cent	0.02	0.46
Tensile strength, lb. per sq. in.	77,700	81,500
Elongation in 8 in., per cent	21	21
Reduction of area, per cent	37	37

The rail steels mentioned above and one high-carbon crucible steel were formed into wires of different diameters, and the properties of the wires were studied by Stead and Wigham.[40] The results indicated that copper had little influence on the tensile strength and elongation of the wires but that it decreased the ductility, as shown by a torsion test and by a bend test. The properties of the wires cold drawn from 0.216 to 0.150 in. are

* The steel was poured into two ladles and copper added to one ladle.

given in Table 41. Data on the properties of the wires in several other conditions were also given. The workmen at the wire mill claimed that the copper-steel wire was "short in the hand"; *i.e.*, it had little toughness as determined by bending the wire by hand.

TABLE 41.—PROPERTIES OF WIRE COLD DRAWN FROM A DIAMETER OF 0.216 TO 0.150 IN.*

Composition, per cent		Torsion in 8 in., twists	Bends of 180 deg. over a radius of 1 cm.	Elongation, per cent†	Tensile strength, lb. per sq. in.
C	Cu				
0.33	0.01	5	4	2.4	127,200
0.32	1.29	4	3	2.0	129,000
0.48	0.03	12	4	2.2	144,200
0.49	0.89	7	2 to 4	2.8	142,900
0.31	0.01	12	4	2.6	134,600
0.29	2.00	7	2 (brittle)	2.8	134,400
0.43	0.02	28	4	2.2	121,200
0.42	0.48	4	2	2.8	141,200
0.99	0.01	2	2	3.8	185,300
0.97	0.46	3	Nil	2.8	182,300

* Stead and Wigham.[40]
† Gage length not given.

Hadfield[42] compared the properties of forging steels containing copper with those of nickel steels. He concluded that copper in percentages necessary to strengthen steel appreciably would cause considerable red-shortness.* Dillner[27] prepared and tested two series of steels, each containing up to 0.6 per cent copper. The materials were tested after annealing and after quenching. It was found that 0.6 per cent copper had no influence on the properties of steel containing 0.1 per cent carbon but that this amount of copper appreciably increased the brittleness of quenched steel containing 1.0 per cent carbon.

Table 42 gives the tensile properties and hardness of three series of copper steels as reported by Breuil[50] in 1907. The specimens were taken from rods rolled from 110-lb. ingots. For alloys of series *A* and *B* the annealing temperature was 900°C. (1650°F.), the quenching temperature 870°C. (1600°F.), and the tempering temperature 300°C. (570°F.). For series *C* these temperatures were 830°C. (1525°F.), 830°C. (1525°F.), and

* See Chap. IV, section D, for contradictory evidence.

TABLE 42.—PROPERTIES OF COPPER STEELS*

Number	Composition, per cent Cu		Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation† in 100 mm., per cent	Reduction of area, per cent	Brinell
Rolled							
A 0	0.17	0.0	72,700	63,500	14.5	52.0	143
A 0.5	0.16	0.49	67,000	55,200	25.5	66.0	146
A 1	0.16	1.00	70,400	59,000	26.5	60.0	146
A 2	0.16	2.01	89,100	67,400	16.0	58.5	202
A 4	0.16	3.98	109,700	98,900	13.0	46.5	255
B 0	0.34	0.0	82,700	53,400	23.2	51.0	166
B 0.5	0.39	0.50	93,200	69,200	20.0	48.5	202
B 1	0.40	1.00	91,800	64,500	20.5	47.3	207
B 2	0.39	2.02	113,300	79,500	11.0	31.5	269
B 4	0.37	4.00	138,200	116,400	11.2	23.5	302
C 0.5	0.57	0.5	118,800	88,400	12.0	22.6	255
C 1	0.56	1.03	127,700	75,900	12.5	16.9	302
C 3	0.60	3.14	161,500	139,900	3.0	2.5	418
C 10	0.72	10.6	178,600	145,400	2.5	1.3	430
Annealed							
A 0	0.17	0.0	55,100	35,900	30.3	63.0	124
A 0.5	0.16	0.49	59,200	38,300	28.0	60.0	143
A 1	0.16	1.00	69,700	54,900	26.0	57.0	146
A 2	0.16	2.01	70,400	58,800	25.0	58.0	174
A 4	0.16	3.98	71,600	65,500	22.0	63.0	183
B 0	0.34	0.0	72,700	45,200	24.0	48.0	166
B 0.5	0.39	0.50	77,900	47,500	23.5	43.0	166
B 1	0.40	1.00	86,200	58,200	20.0	40.0	196
B 2	0.39	2.02	87,700	64,900	18.0	40.0	207
B 4	0.37	4.00	97,500	80,400	16.0	42.0	212
C 0.5	0.57	0.50	102,700	58,300	16.5	42.7	228
C 1	0.56	1.03	107,400	60,200	8.5	18.2	223
C 3	0.60	3.14	115,500	76,800	7.5	20.6	223
C 10	0.72	10.6	117,400	92,800	10.0	30.0	241
Quenched in water							
A 0	0.17	0.0	97,500	70,700	14.5	67.0	207
A 0.5	0.16	0.49	95,300	70,700	16.0	52.7	311
A 1	0.16	1.00	132,000	118,100	5.5	26.2	311
A 2	0.16	2.01	159,400	150,800	5.2	25.6	311
A 4	0.16	3.98	196,400	150,800	7.0	29.5	351
B 0	0.34	0.0	144,400	116,000	2.5	0.1	460
B 0.5	0.39	0.50	108,900	108,900	1.4	0.0	627
B 1	0.40	1.00	145,900	145,900	1.4	0.0	600
B 2	0.39	2.02	106,700	106,700	1.4	0.0	817
B 4	0.37	4.00	142,600	142,600	1.4	0.0	782
Quenched and tempered							
A 0	0.17	0.0	91,100	65,700	10.5	68.0	192
A 0.5	0.16	0.49	102,700	72,900	8.5	60.0	311
A 1	0.16	1.00	98,200	75,100	11.5	66.0	277
A 2	0.16	2.01	158,000	145,900	6.5	33.8	345
A 4	0.16	3.98	142,300	121,700	11.0	52.0	325
B 0	0.34	0.0	141,600	103,600	7.5	33.2	418
B 0.5	0.39	0.50	197,800	192,400	3.5	18.0	460
B 1	0.40	1.00	230,800	212,000	3.5	7.5	495
B 2	0.39	2.02	237,600	220,800	2.0	1.5	495
B 4	0.37	4.00	246,200	224,800	1.5	1.0	782

* Breuil.[50]
† Specimen 13.8 mm. (0.54 in.) diameter and 100 mm. (3.93 in.) long.

350°C. (660°F.) respectively. Steels of series *C*, containing 0.6 per cent carbon, cracked badly when quenched in water. As the data in Table 42 show, copper, when present in amounts greater than 0.5 per cent, increased the strength of steels of each series, but its influence was much more pronounced in the as-rolled than in the annealed samples. The comparatively high strength of steel *A* 0 in the as-rolled condition was ascribed to finishing the hot rolling at a low temperature. Torsional tests and a non-standard type of shock test were also made.

Breuil also studied the influence of copper on the properties of steel containing 1 per cent carbon. As in the case of steels of lower carbon content, copper increased the strength of this steel in the as-rolled and in the normalized condition. The influence of copper, up to 3 per cent, on the properties of the steel quenched in hot water was uncertain; the Brinell hardness of the quenched steels was not over 332. Lathe tools were made from the 1 per cent carbon steels containing nil, 1, and 3 per cent copper. These tools were quenched in cold water and their life was determined for turning bars of a 0.7 per cent carbon steel. The weight of metal removed by each tool, as is shown below, indicated that copper had little influence on the cutting ability of the steel.

Steel	Weight of turnings removed, kg.	Weight of turnings removed, lb.
No copper.....	0.924	2.032
1 per cent copper	1.075	2.365
3 per cent copper	1.065	2.343

Wrought steels containing approximately 0.4 per cent carbon and as much as 4 per cent copper were tested by Clevenger and Ray.[70] In agreement with earlier investigators, they found that copper increased the strength of the material in both the as-forged and annealed condition, but the strengthening effect was greatest in the unannealed material.

87. Work of Bird.—Some results obtained by R. M. Bird of the Bethlehem Steel Company and assembled in 1922 show the superimposition of softening by tempering and hardening by precipitation when quenched copper steels are tempered at temperatures which bring about precipitation hardening. Fig-

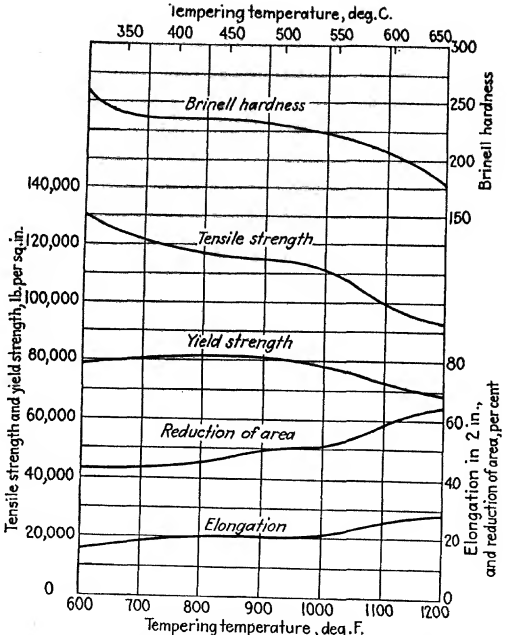


FIG. 89.—Properties of a steel containing 0.34 per cent carbon and 0.57 per cent copper, quenched in water from 815°C. (1500°F.) and tempered at the indicated temperatures. (*Bird.*)

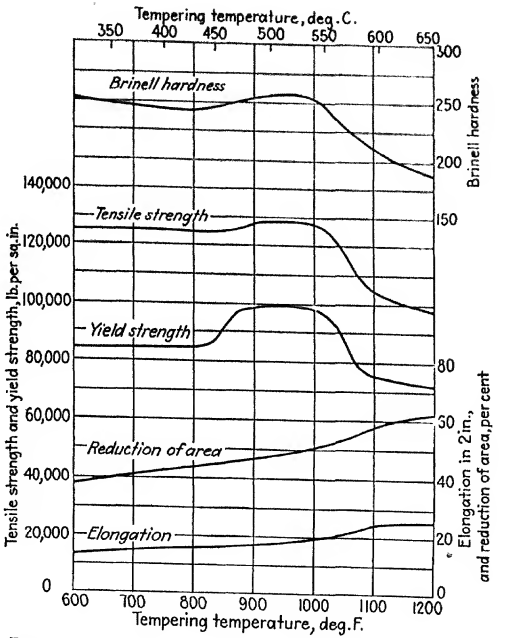


FIG. 90.—Properties of a steel containing 0.25 per cent carbon and 1.05 per cent copper, quenched in water from 815°C. (1500°F.) and tempered at the indicated temperatures. (*Bird.*)

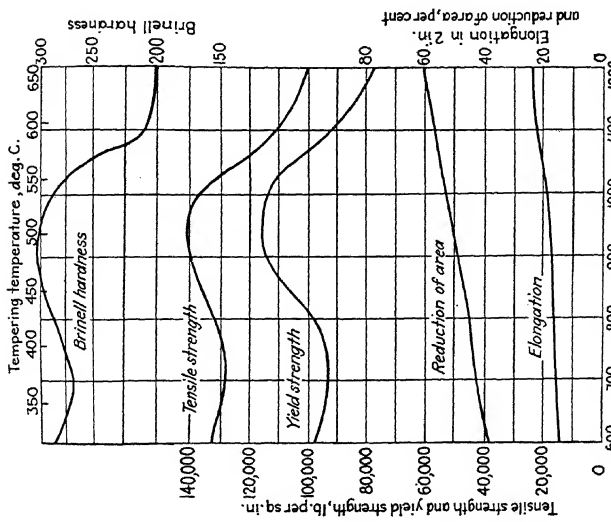


FIG. 91.—Properties of a steel containing 0.34 per cent carbon and 2.10 per cent copper, quenched in water from 815°C. (1500°F.) and tempered at the indicated temperatures. (*Bird.*)

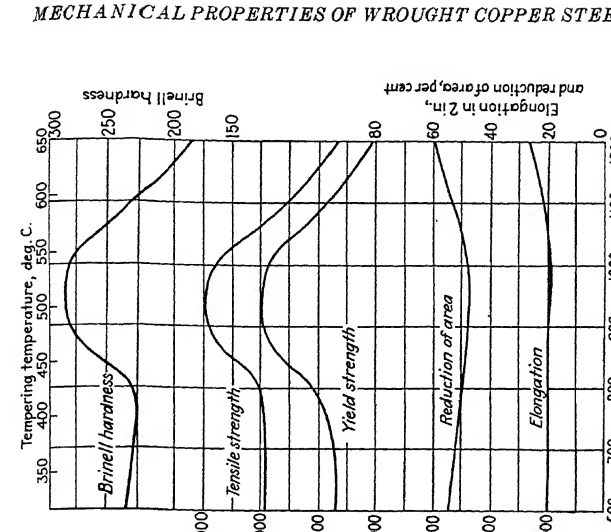


FIG. 92.—Properties of a steel containing 0.34 per cent carbon and 3.11 per cent copper, quenched in water from 815°C. (1500°F.) and tempered at the indicated temperatures. (*Bird.*)

ures 89 to 92 show the influence of tempering temperature on the properties of water-quenched steels containing approximately

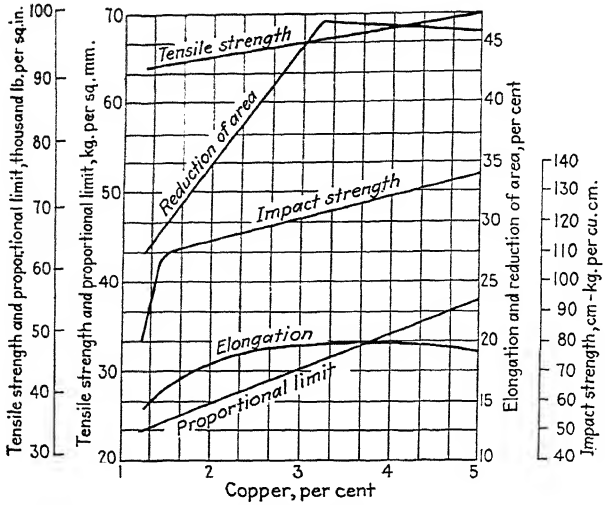


FIG. 93.—Influence of copper on the properties of a 1.1 per cent carbon steel, annealed to yield spheroidized cementite. (*Stogoff and*

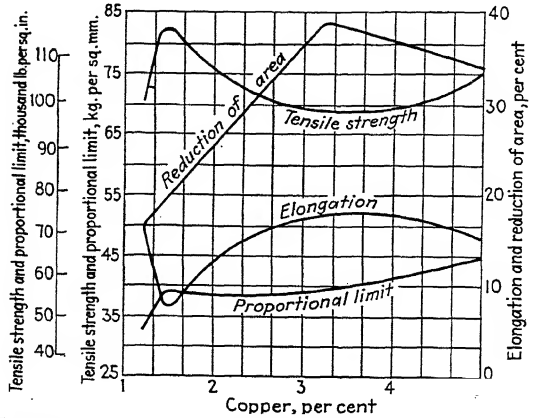


FIG. 94.—Influence of copper on the properties of a 1.1 per cent carbon steel, annealed to yield lamellar pearlite. (*Stogoff and Messkin.*[219])

0.30 per cent carbon and from 0.57 to 3.11 per cent copper. The specimens as treated were in the form of 1-in. rounds that had

been rolled from 5-in. ingots. The tensile- and yield-strength curves for the steels containing 1.05, 2.10, and 3.11 per cent cop-

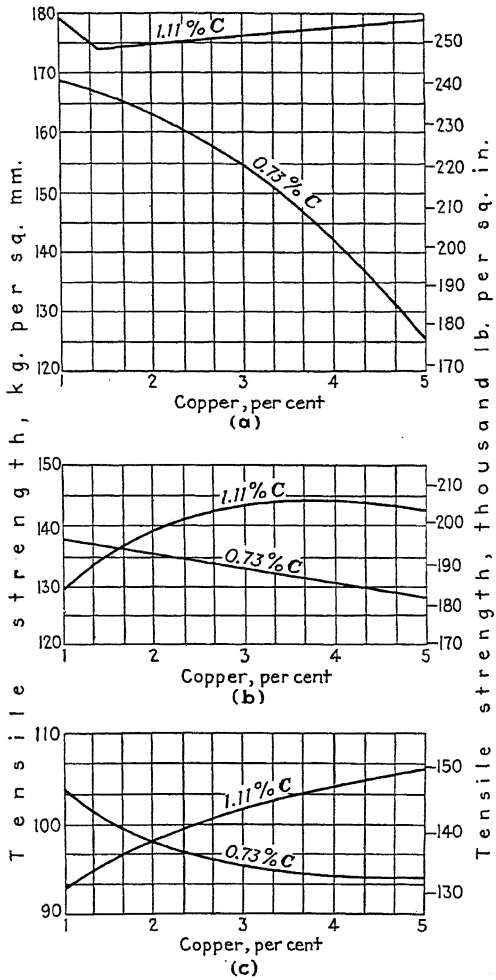


FIG. 95.—Tensile strength of copper steels with 0.73 and 1.1 per cent carbon, quenched in oil from 800°C. (1470°F.) and tempered at (*a*) 400°C. (750°F.), (*b*) 500°C. (930°F.), and (c) 600°C. (1110°F.). (*Stogoff and Messkin.*[219])

per showed a "hump" in the neighborhood of 500°C. (930°F.), which can be attributed to precipitation hardening during

tempering. The hump is absent in the steel containing only 0.57 per cent copper, as is to be expected.

88. Stogoff and Messkin's Work.—The properties of eight high-carbon steels containing from 1.2 to 5 per cent copper were studied by Stogoff and Messkin.[219] They did not determine the

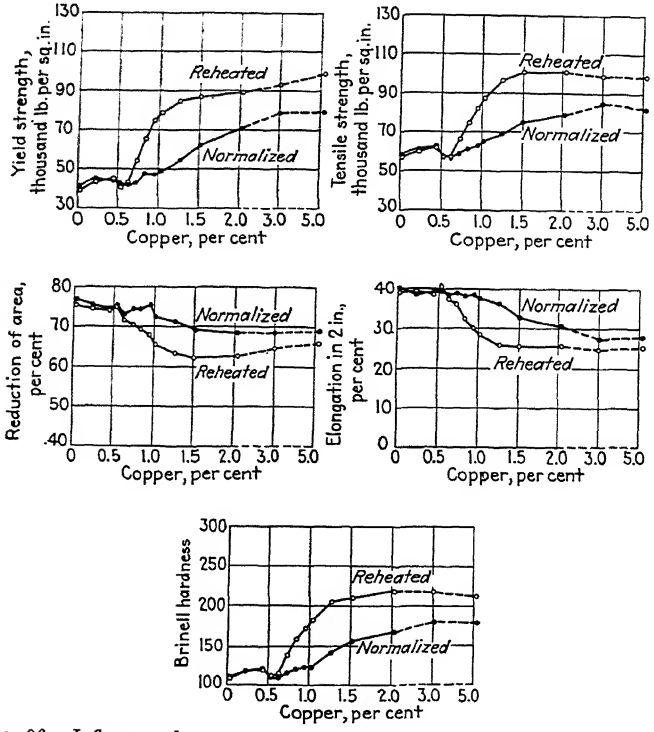


FIG. 96.—Influence of copper content on the mechanical properties of 0.05 to 0.08 per cent carbon steels, normalized from 900°C. (1650°F.) and reheated 4 hr. at 500°C. (930°F.). (*Smith and*

mechanical properties of copper-free steels, and it is, therefore, difficult to determine from their work just how greatly the steels were influenced by the copper. The effect of from 1.2 to 5 per cent copper on the tensile properties and impact resistance of steels containing 1.1 per cent carbon that had been annealed to spheroidize the cementite is shown by Fig. 93. Figure 94 shows the influence of copper on the same steels annealed to produce lamellar pearlite.

TABLE 43.—PROPERTIES OF QUENCHED AND QUENCHED AND TEMPERED COPPER STEELS*

Steel number	Composition, per cent		Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation,† per cent	Brinell hardness
	C	Cu				
Quenched in oil from 800°C. (1470°F.)						
1	0.87	1.19	124,500	.....	....	363
2	0.76	3.03	57,900	.....	....	712
3	0.69	4.81	84,800	.....	....	415
4	1.11	1.42	78,700	.....	....	682
5	1.07	3.25	98,900	.....	....	682
6	1.03	5.07	92,500	.....	....	653
7	0.74	1.41	96,200			
8	1.22	1.27	121,300	.....	....	653
Tempered at 400°C. (750°F.)						
1	0.87	1.19	231,900	169,300	7.5	
2	0.76	3.03	219,100	190,700	4.4	
3	0.69	4.81	182,100			
4	1.11	1.42	247,600	205,000	1.8	
6	1.03	5.07	254,800	207,700	5.1	
7	0.74	1.41	237,600	195,000	3.9	
8	1.22	1.27	250,400	210,500	1.9	
Tempered at 500°C. (930°F.)						
1	0.87	1.19	177,100	148,700	8.3	
2	0.76	3.03	187,100	156,800	8.8	
3	0.69	4.81	183,000	149,500	8.4	
4	1.11	1.42	192,100	148,500	6.3	
5	1.07	3.25	204,900	155,800	6.1	
6	1.03	5.07	203,500	167,200	7.3	
7	0.74	1.41	194,900	155,800	10.0	
8	1.22	1.27	189,200	159,200	4.7	
Tempered at 600°C. (1110°F.)						
1	0.87	1.19	124,200	103,400	13.0	
2	0.76	3.03	135,100	104,700	11.3	
3	0.69	4.81	133,500	106,700	9.7	
5	1.07	3.25	145,500	125,200	7.3	
6	1.03	5.07	150,800	135,200	5.7	
7	0.74	1.41	143,700	124,500	13.2	
8	1.22	1.27	134,600	126,000	7.3	

* Stogoff and Messkin.[219]

† $l = 11d$.

The properties of the steels quenched in oil from 800°C. (1470°F.) and as quenched from this temperature and then tempered are given in Table 43. As the copper content of tempered steels containing 0.7 per cent carbon increased from 1.2 to 5 per cent, the tensile strength gradually decreased. With steels containing 1.1 per cent carbon, however, the strength

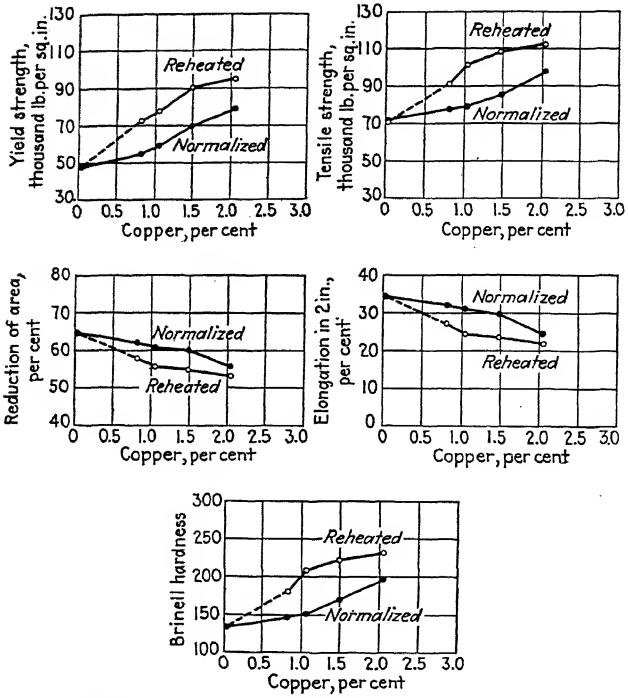


FIG. 97.—Influence of copper content on the mechanical properties of 0.20 per cent carbon steel, normalized at 865°C. (1590°F.) and reheated 4 hr. at 500°C. (930°F.). (*Smith and Palmer.*[378])

tended to increase as the copper increased from 1.2 to 5 per cent. These observations are pictured by the curves of Fig. 95.

Stogoff and Messkin also found that copper tended to increase the depth of hardening on quenching.

89. Nehl's Work.—Some of Nehl's[267] findings regarding precipitation hardening and cast steels were discussed in Chapters VI and VII. He also determined the properties of copper-steel plates containing approximately 1 per cent copper. Table 44,

TABLE 44.—PROPERTIES OF PLATES OF A COPPER STEEL CONTAINING 0.12 PER CENT CARBON AND 0.85 PER CENT COPPER*

Plate thickness		Condition	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation,‡ per cent	Impact resistance, m-kg. per sq. cm.
mm.	in.					
10	0.39	As rolled	68,200	46,200	23.5	16.0
10	0.39	Reheated†	88,900	74,700	16.8	15.4
15	0.59	As rolled	66,100	44,100	26.2	18.0
15	0.59	Reheated†	85,400	66,200	17.3	13.8
20	0.79	As rolled	64,700	51,900	25.5	19.0
20	0.79	Reheated†	83,600	64,000	17.0	15.4

* Nehl.[267]
† 500°C. (930°F.) for 1 hr.
‡ $l = 11.3\sqrt{A}$.

selected from Nehl, gives the properties of copper-steel plate containing 0.12 per cent carbon, 0.65 per cent manganese, and 0.85 per cent copper. The rolling of the plates was completed at a temperature above 900°C. (1650°F.), and the reheated specimens were held at 500°C. (930°F.) for 1 hr. Impact tests for the 10-mm. (0.39-in.) plate were made on notched specimens having a cross-section of 10 × 15 mm. (0.39 × 0.59 in.), and those for the heavier plates were made on 15 × 15-mm. (0.59 × 0.59-in.) specimens. Elongation was determined over a gage length 11.3 times the square root of the cross-sectional area.

As may be observed from Table 44, precipitation hardening on reheating increased the tensile strength 30 per cent and the yield strength by at least 50 per cent. Precipitation hardening decreased the elongation 30 per cent and the impact resistance from 4 to 23 per cent. According to Nehl, with other low-alloy steels it was necessary to resort to a quenching treatment in order to produce sheet with properties as good as shown by the reheated plates of copper steel.

Table 45 gives the properties of shafting of three sizes both as forged and after reheating the forged material. The steel was from the heat mentioned above (0.12 per cent carbon and 0.85 per cent copper). Even the shaft 300 mm. (11.8 in.) in diameter was hardened by the precipitation-hardening treat-

TABLE 45.—PROPERTIES OF COPPER STEEL SHAFTING*

Diameter		Condition†	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, per cent‡	Reduction of area, per cent	Impact resistance,§ m-kg. per sq. cm.
mm.	in.						
100	3.9	R	70,100	51,200	24.6	65	10.4
100	3.9	T	82,800	66,200	19.6	59	6.0
200	7.9	R	67,300	46,200	25.2	65	9.5
200	7.9	T	83,300	62,300	20.0	59	4.6
300	11.8	R	66,600	45,200	25.8	66	9.3
300	11.8	T	77,700	58,600	17.4	57	3.3

* Nehl.(267)

† R—as rolled; T—reheated at 450 to 500°C. (840 to 930°F.) for 5 hr.

‡ $l = 11.3\sqrt{A}$.

§ 10 × 10 × 60-mm. samples with keyhole notch 5 mm. deep.

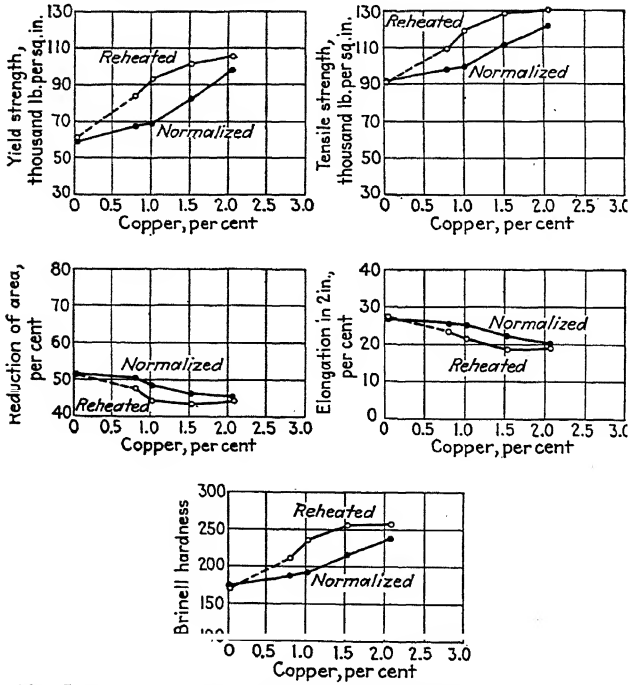


FIG. 98.—Influence of copper content on the mechanical properties of 0.43 per cent carbon steel, normalized at 865°C. (1590°F.) and reheated 4 hr. at 500°C. (930°F.). (*Smith and Palm*—(278))

ment, but it did not reach so high a strength as the shafts of smaller diameter.

90. Work of Smith and Palmer.—These investigators paid particular attention to the improvement of copper steels by a precipitation-hardening treatment. The steels used were made in 12-lb. lots and were forged into 0.75-in. rounds. All

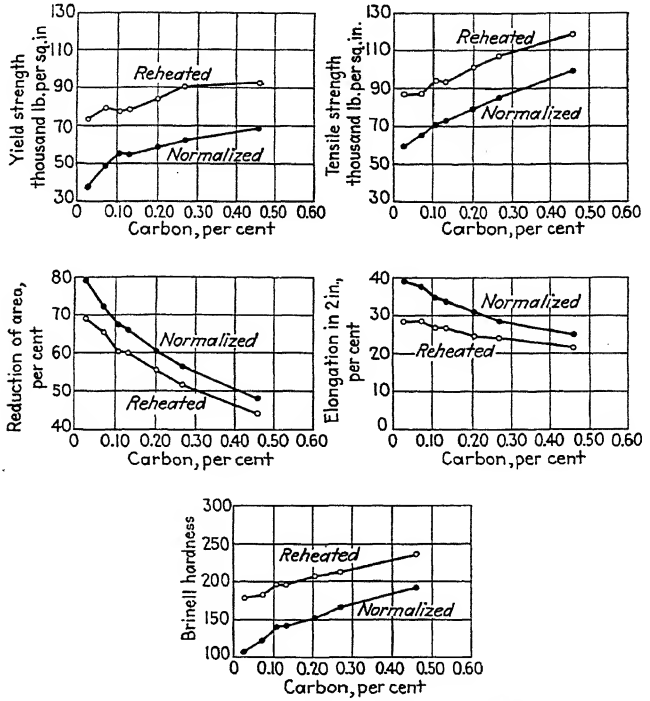


FIG. 99.—Influence of carbon content on the mechanical properties of normalized and reheated steels containing 1.02 per cent copper. (*Smith and Palmer.*[378])

steels contained approximately 0.5 per cent manganese, and the silicon content ranged from 0.05 to 0.10 or 0.15 per cent. They were "killed" with 0.025 per cent aluminum. All of the steels were normalized, and tensile tests were made on both normalized samples and samples normalized and then reheated at 500°C. (930°F.) for 4 hr.

Some of Smith and Palmer's data on the properties of normalized and reheated steels are shown in Figs. 96 to 99. As these

figures show, the copper content increases the strength of the normalized materials, and when 1 per cent or more copper is present reheating increases the strength by approximately 20,000 lb. per sq. in.

Figure 100 shows the properties of a 0.20 per cent carbon steel with varying copper contents quenched in oil from 900°C.

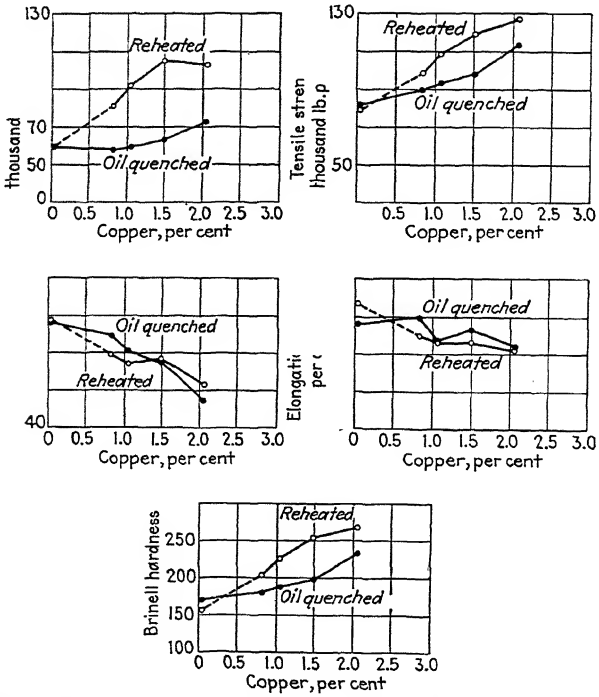


FIG. 100.—Influence of copper content on the mechanical properties of 0.20 per cent carbon steel, quenched in oil from 900°C. (1650°F.) and reheated 4 hr. at 500°C. (930°F.). (*Smith and Palmer.*[373])

(1650°F.) and then reheated at 500°C. (930°F.), while Fig. 101 shows the properties of the same steel furnace cooled from 800°C. (1470°F.) and then reheated to 500°C. (930°F.). Precipitation hardening occurred in even the slowly cooled specimens containing 0.8 per cent or more copper.

Table 46 gives the properties of copper steels hardened by the direct-precipitation treatment mentioned on page 153. The

TABLE 46.—TENSILE PROPERTIES OF COPPER STEELS GIVEN A DIRECT-PRECIPITATION TREATMENT WITHOUT INTERMEDIATE COOLING TO ROOM TEMPERATURE*

Heat treatment	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell hardness
1.06 per cent copper, 0.061 per cent carbon					
1. Air cooled to room temperature after 1 hr. at 865°C. (1590°F.)	60,900	48,400	38.0	74.4	123
2. Same as 1, then reheated for 4 hr. at 500°C. (930°F.)	85,800	73,900	28.0	67.0	187
3. 1 hr. at 800°C. (1470°F.), cooled in salt bath at 500°C. (930°F.), held 4 hr. at 500°C. (930°F.)	85,100	71,850	29.3	67.5	184
4. 1 hr. at 800°C. (1470°F.), air cooled to 500°C. (930°F.), placed in furnace at 500°C. (930°F.), and held 4 hr	85,100	70,000	29.0	67.2	183
5. Same as 4, but held at 500°C (930°F.) for 2 hr	81,900	68,400	31.0	67.5	170
6. Same as 4, but held at 500°C. (930°F.) for 1 hr	74,900	64,900	32.0	69.1	153
1.07 per cent copper, 0.193 per cent carbon					
1. Air cooled to room temperature after 1 hr. at 865°C. (1590°F.)	71,600	51,900	32.5	60.1	143
2. Same as 1, then reheated for 4 hr. at 500°C. (930°F.)	95,000	75,900	25.0	55.6	207
3. 1 hr. at 800°C. (1470°F.), cooled in salt bath at 500°C. (930°F.), held 4 hr. at 500°C. (930°F.)	95,900	74,150	26.2	57.0	198
4. 1 hr. at 800°C. (1470°F.), air cooled to 500°C. (930°F.), placed in furnace at 500°C. (930°F.), and held 4 hr	95,600	74,150	25.8	54.9	198
5. Same as 4, but held at 500°C. (930°F.) for 2 hr	92,600	72,400	26.5	55.2	186
6. Same as 4, but held at 500°C. (930°F.) for 1 hr	85,200	64,100	28.5	56.9	170

* Smith and Palmer.[378]

same properties were obtained by the interrupted cooling as by cooling to ordinary temperature and then reheating.

Figure 102 shows the properties as a function of the reduction by cold rolling for sheet containing 0.07 per cent carbon and 1.02 per cent copper. Sheets of different gages were normalized and then cold-rolled to 0.040 in., the gage of the finished sheet.

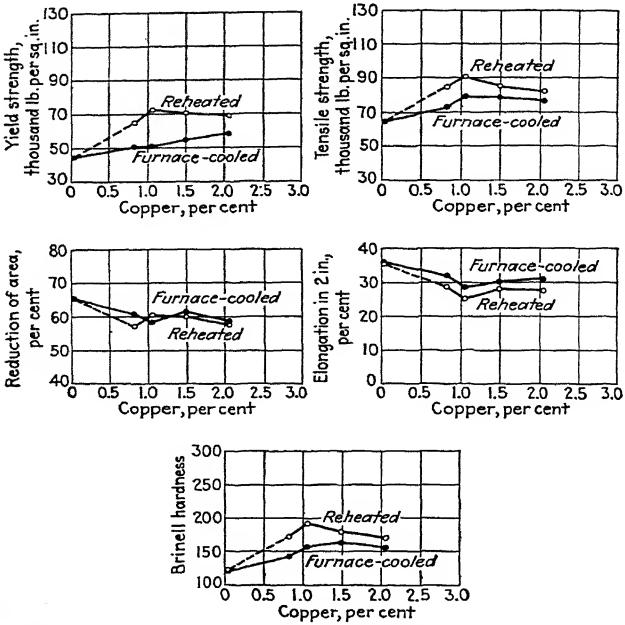


FIG. 101.—Influence of copper content on the mechanical properties of 0.20 per cent carbon steel, furnace cooled from 800°C. (1470°F.) at the rate of 100°C. (180°F.) per hour and reheated 4 hr. at 500°C. (930°F.). (*Smith and Palmer.*[378])

After reheating, the specimens that received 0 and 10 per cent reduction are found to have hardened appreciably, but with 50 per cent reduction, although the hardness increases, the yield point of the rolled material is barely maintained, and the strength of the 75 per cent reduction specimen actually decreases except at the lowest temperatures of reheating. Of very great interest is the marked improvement in ductility which occurs without loss of strength when the cold-worked specimens are reheated. This is reflected by an increase of the Erichsen

value from 0.304 to 0.330 and from 0.210 to 0.230 in. respectively for the 10 and 50 per cent reduction samples after reheating at 450°C. (840°F.).

Unpublished work of Smith and Palmer has, however, shown that in the presence of carbon the strength of cold-drawn wire decreases on reheating.

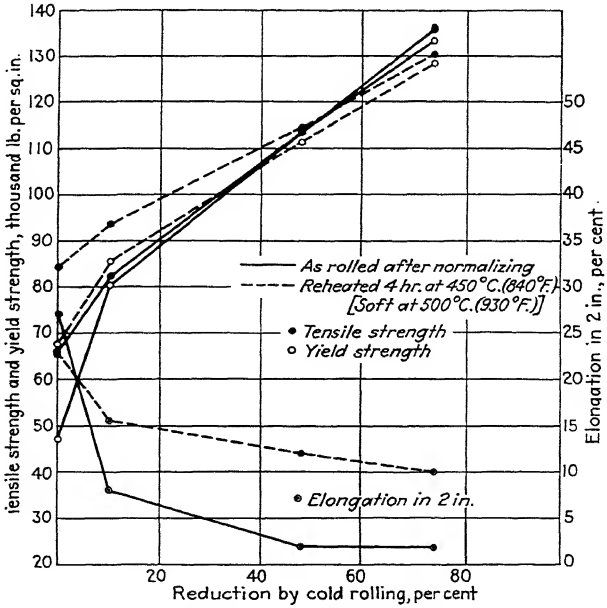


FIG. 102.—Properties of 0.07 per cent carbon, 1.02 per cent copper steel sheet, normalized, cold-rolled to the reductions shown, and then reheated at 500°C. (930°F.) for 4 hr.

91. Work of Lorig and MacLaren.—Some of the more important results of these investigators are summarized in Figs. 103 to 106, which show the properties of steels of varying carbon and copper contents that had been given different heat treatments. All of the data were obtained from heats made on a laboratory scale. The alloys were forged and rolled into bars approximately 1 in. in diameter. The curves in the figures so clearly picture the influence of copper in the steels of different carbon content that discussion of the results seems unnecessary.

B. PROPERTIES AT ELEVATED TEMPERATURES

The data on the high-temperature properties of cast steels given in Chapter VII show that for temperatures below 400°C. (750°F.) copper increases the strength of low-carbon steel. Some data on the influence of copper on the high-temperature properties of wrought steels are given below.

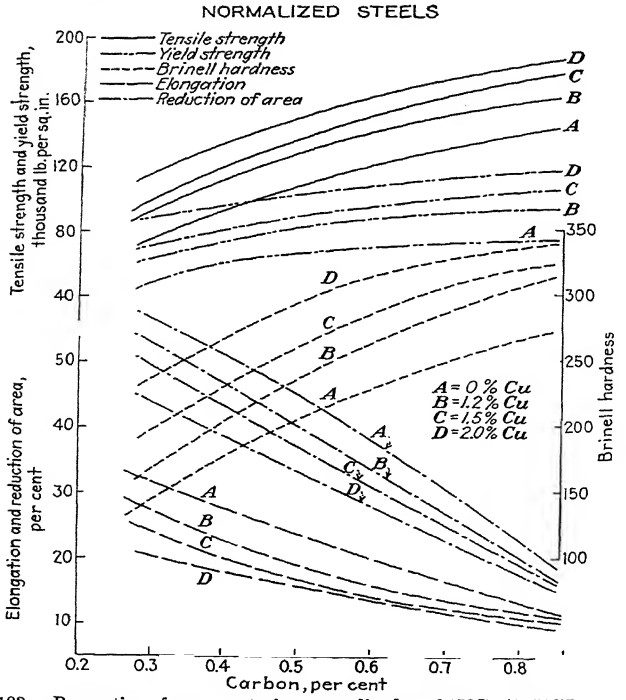


FIG. 103.—Properties of copper steels, normalized at 845°C. (1550°F.). (*Lorig and MacLaren.*)

92. Properties Obtained by Short-time Tests.—Table 47, from Nehl,[267] shows short-time tensile values for a plate of copper steel at temperatures up to 500°C. (930°F.) and, for comparison, similar values for a plate of carbon steel having the same strength at ordinary temperature as the copper steel. The plates were 20 mm. (0.79 in.) thick and were evidently tested in the

TABLE 47.—TENSILE PROPERTIES OF A CARBON-STEEL PLATE AND COPPER-STEEL PLATE AT ELEVATED TEMPERATURES*

Temperature		Steel†	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation,‡ per cent	Reduction of area, per cent
°C.	°F.					
20	70	*A*	67,600	32,200	20.7	55.7
20	70	*B*	67,500	47,500	26.0	61.0
100	210	*A*	62,900	31,200	15.5	54.0
100	210	*B*	66,200	43,000	18.3	45.5
200	390	*A*	75,100	31,900	12.4	39.6
200	390	*B*	81,100	42,100	17.2	42.3
300	570	*A*	73,100	24,000	22.4	48.0
300	570	*B*	78,000	34,300	22.5	40.6
400	750	*A*	54,800	24,500	21.6	59.9
400	750	*B*	61,900	31,600	28.5	52.5
500	930	*A*	33,900	13,700	26.4	72.0
500	930	*B*	42,100	25,800	26.7	48.2

* Nehl.[267]

† Steel: *A*—0.29 per cent carbon, 0.60 per cent manganese, and 0.14 per cent copper.
B—0.11 per cent carbon, 0.65 per cent manganese, and 0.85 per cent copper.

‡ Gage length of eleven times square root of cross-sectional area.

TABLE 48.—STEELS TESTED BY POMP AND ENDERS[331]

Designation	Composition, per cent								
	C	Si	Mn	P	S	Cr	Ni	Mo	Cu
C1	0.08	0.09	0.47	0.015	0.033				
C2	0.37	0.31	0.67	0.027	0.028				
Ni	0.18	0.19	0.74	0.016	0.021	0.18	1.56		
Mo	0.14	0.08	0.43	0.024	0.027	0.03	0.20	0.30	
Mo-Cu	0.13	0.15	0.86	0.017	0.019	....	....	0.25	0.19
Cr-Mo	0.12	0.28	0.29	0.012	0.014	0.71	0.30	0.30	
Cu	0.09	0.19	0.56	0.021	0.029	....	....	....	0.83

as-rolled condition. Tests on the carbon steel were made by Körber and Pomp.[185] At all temperatures the yield strength (0.2 per cent elongation) of the copper steel was above that of the carbon steel, and for elevated temperatures the tensile strength of the copper steel was above that of the carbon steel. Nehl concluded that the values obtained proved that copper steel would be a desirable material for boiler construction.

Again, it may be well to point out that the properties of copper steel are not stable at temperatures above 400°C. (750°F.) because the copper tends to precipitate and agglomerate and thereby causes the steel to soften as it is held at a high temperature.

In investigating the properties of low-alloy steels suitable for the construction of superheaters, Pomp and Enders[331] used the steels whose compositions are given in Table 48. The short-time tensile properties of the two carbon steels and the copper steel are

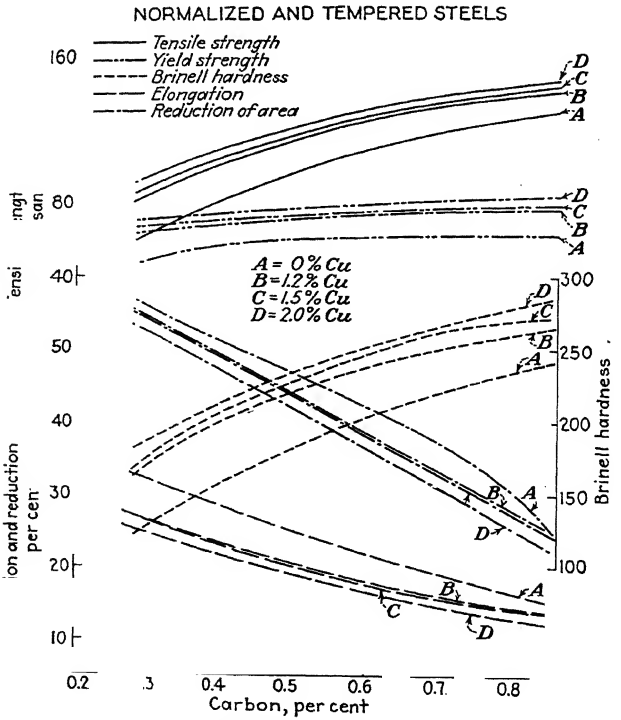


FIG. 104.—Properties of copper steels, normalized at 845°C. (1550°F.) and tempered at 650°C. (1200°F.) for 1 hr. (*Lorig and MacLaren.*)

shown in Fig. 107, where the yield strength shown is that for an elongation of 0.2 per cent. The minima in the elongation and reduction-of-area curves at 550°C. (1020°F.) for the copper steel can probably be attributed to precipitation of copper at the testing temperature. Accelerated creep tests were also made on these steels, the results of which will be given in the next section.

Figure 108 by Lorig and MacLaren shows the tensile properties at elevated temperatures of three copper steels and unalloyed steels of the same carbon content. All samples were normalized at 850°C. (1560°F.). According to the data shown, copper in these steels of comparatively high carbon content reduced the

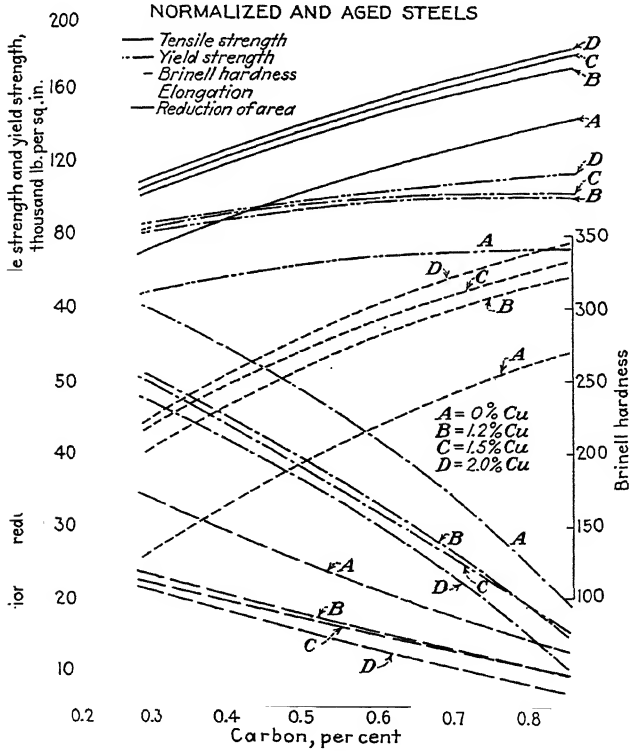


FIG. 105.—Properties of copper steels normalized at 865°C. (1590°F.) and reheated at 500°C. (930°F.) for 4 hr. (*Lorig and MacLaren.*)

ductility at elevated temperatures but had little influence on tensile strength.

93. So-called Creep Limits.—The only creep data for copper steels are those published by Pomp and Enders,[331] which were obtained by means of a greatly accelerated test and do not really correspond to creep data as the expression is now understood. The tests were made on the steels described in Table 48, and the

stresses required to produce elongation at the rate of 0.003 per cent per hr. between the fifth and tenth hour are shown as a function of the temperature in Fig. 109. According to these results, the creep strength of copper steel at temperatures up to 600°C. (1110°F.) is appreciably greater than that of carbon steel.

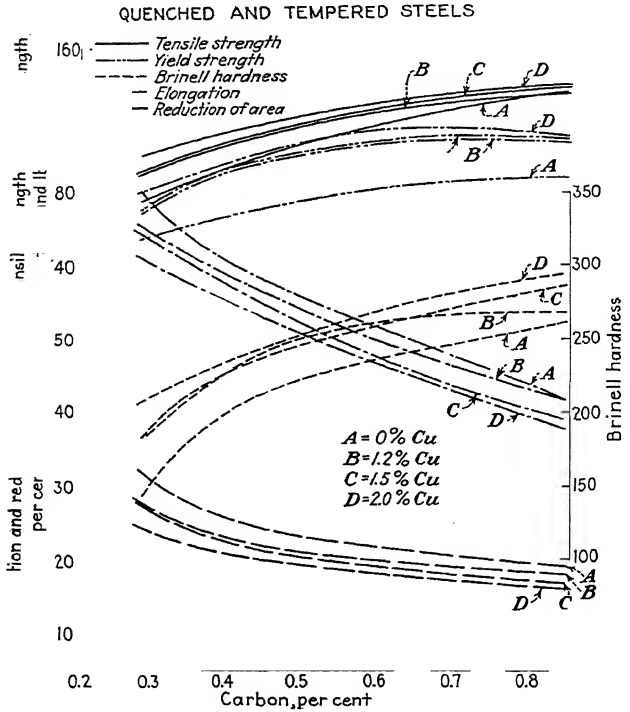


FIG. 106.—Properties of copper steels, quenched in oil from 845°C. (1550°F.) and tempered at 650°C. (1200°F.) for 1 hr. (*Lorig and MacLaren.*)

In a letter commenting on the first draft of this monograph C. H. Desch wrote that in some experiments on creep made at the National Physical Laboratory "no advantage was found by the addition of copper to a carbon steel, but the number of experiments is small."

C. SPECIAL PROPERTIES

The effect of copper on fatigue resistance and notched-bar impact resistance as influenced by testing temperature and special treatment is discussed below.

TABLE 49.—ENDURANCE PROPERTIES OF CARBON AND COPPER STEELS*

Composition, per cent				Heat treatment	Endurance limit, lb. per sq. in. (A)	Tensile strength, lb. per sq. in. (B)	Endurance ratio $\frac{A}{B}$
C	Si	Mn	Cu				
0.61	0.16	0.55	0.07	N	48,000	104,000	0.46
0.61	0.16	0.55	0.07	R	47,000	106,500	0.44
0.59	0.16	0.51	1.13	N	55,000	114,500	0.48
0.59	0.16	0.51	1.13	R	65,000	132,500	0.49
0.57	0.16	0.51	1.65	N	61,000	113,000	0.54
0.57	0.16	0.51	1.65	R	71,000	137,000	0.52
0.60	0.28	0.78	1.49	N	65,000	140,000	0.46
0.60	0.28	0.78	1.49	R	71,000	152,000	0.47

* Lorig and MacLaren.
N—Normalized at 850°C. (1560°F.).
R—Normalized and then reheated 4 hr. at 500°C. (930°F.).

94. Fatigue Resistance.—Endurance values of three copper steels and one carbon steel obtained by Lorig and MacLaren are given in Table 49, and stress-cycle curves for two of the steels are shown in Fig. 110. These data indicate that the addition of copper to steel of a comparatively high carbon content does not change the endurance ratio and that the increase in tensile strength brought about by the copper is accompanied by the same percentage increase in fatigue limit. Precipitation hardening increases the endurance limit, and the percentage increase is the same as the percentage increase in tensile strength, according to the data in Table 49.

McAdam[187] found that the addition of 1 per cent copper to a steel containing 0.15 per cent carbon increased the endurance limit as determined in air but that it had no influence on the resistance to corrosion fatigue.

Gough[318] also found that steel containing 1 per cent copper, as well as other low-alloy steels, had the same resistance to corrosion fatigue as carbon steels. Schulz and Buchholtz,[303] however, cited data to prove that copper-chromium structural steel had a greater resistance to corrosion fatigue than a structural silicon steel.

95. Impact Resistance at Different Temperatures.—Yamada[174] made impact tests on a number of carbon and alloy steels at temperatures as low as −190°C. (−310°F.). One of the steels contained 0.29 per cent carbon and 1 per cent copper.

The notched-bar impact resistance of this steel in the annealed condition was 7.7 m-kg. per sq. cm. at 20°C. (70°F.) and only 0.2 m-kg. per sq. cm. at −190°C. (−310°F.). The results indicated that copper had little influence on the drop in impact

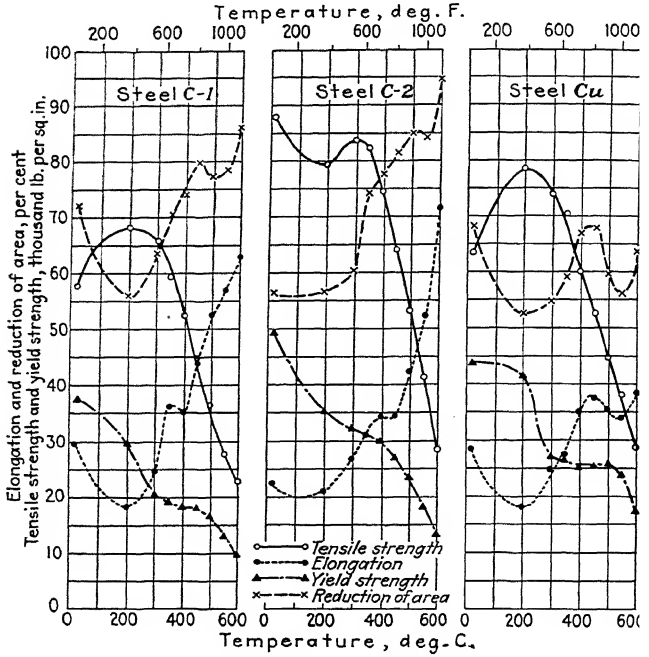


FIG. 107.—Tensile properties of the following steels at elevated temperatures:

Steel	Composition, per cent		
	C	Mn	Cu
C-1	0.08	0.47	
C-2	0.37	0.67	
Cu	0.09	0.56	0.83

(*Pomp and Enders.*[331])

resistance as the temperature was lowered. Results given in Chapter XI, however, indicate that copper-chromium steels have a high impact resistance at subatmospheric temperatures.

The effects of artificial aging on the impact resistance of a copper steel as determined by Nehl[267] are given in Table 50. The steel contained 0.11 per cent carbon and 0.85 per cent copper.

TABLE 50.—EFFECT OF ARTIFICIAL AGING ON THE IMPACT RESISTANCE OF A COPPER STEEL*

Condition	Unaged, impact resistance, m-kg. per sq. cm.	Aged, impact resistance, m-kg. per sq. cm.	Percentage decrease on aging
10-mm. plate as rolled	19.8	14.5	27
15-mm. plate as rolled	20.3	11.0	46
20-mm. plate as rolled	16.7	1.8	89
10-mm. plate reheated to 650°C. (1200°F.)	24.3	18.4	24
15-mm. plate reheated to 650°C. (1200°F.)	22.9	11.2	51
20-mm. plate reheated to 650°C. (1200°F.)	20.2	8.0	60
10-mm. plate normalized at 900°C. (1650°F.)	23.9	16.4	31
15-mm. plate normalized at 900°C. (1650°F.)	22.7	12.7	44
20-mm. plate normalized at 900°C. (1650°F.)	21.2	11.6	45
10-mm. plate normalized and then reheated to 650°C. (1200°F.)	24.4	18.0	26
15-mm. plate normalized and then reheated to 650°C. (1200°F.)	24.0	13.6	48
20-mm. plate normalized and then reheated to 650°C. (1200°F.)	24.3	13.6	44

* Nehl.[267]

"Aging" consisted in elongating 10 per cent and then heating to 250°C. (480°F.).

These data certainly indicate that the steel was sensitive to aging, yet Nehl claimed that they show it to be less susceptible to aging than unalloyed steel made by the same process (open-hearth).

Figure 111, from Nehl,[267] shows temperature-impact-resistance curves for a steel containing 0.12 per cent carbon and 0.85 per cent copper. Precipitation hardening induced by reheating to 525°C. (975°F.) shifted the steep portion of the curves to higher temperatures and thereby decreased impact resistance at ordinary temperature. By finishing the rolling at a low temperature the steep portions of the curves were shifted to lower temperatures.

Respek[371] recently mentioned a "Cuprizett" steel containing from 0.25 to 0.50 per cent copper, which was claimed to have the non-aging characteristics of "Izett" steel and the corrosion resistance of the standard copper-bearing steel.

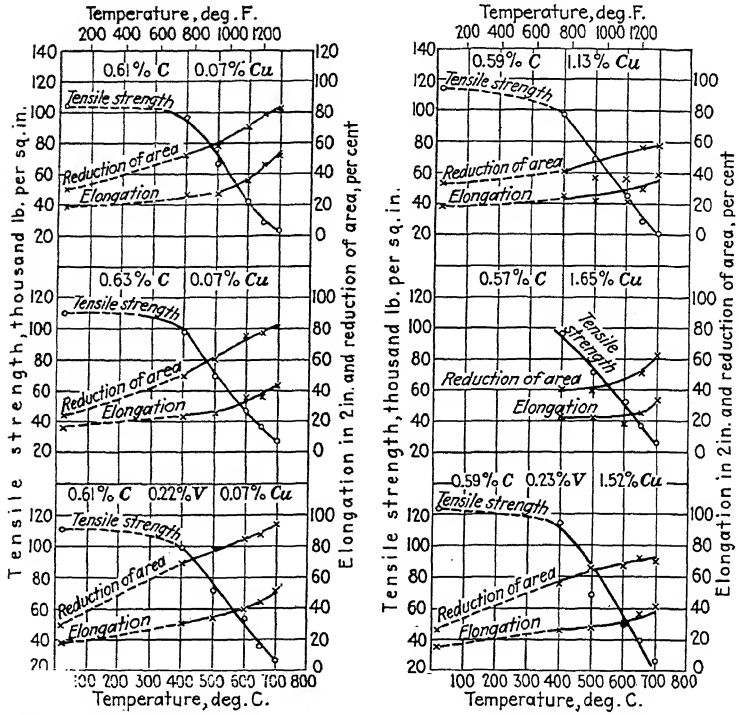


FIG. 108.—Tensile properties of normalized steels at elevated temperatures. (*Lorig and MacLaren.*)

D. AUTHORS' SUMMARY

1. Copper, like many other alloys used in steel, increases strength and hardness of steels of low and medium carbon content. The increase in strength brought about by copper is greater in as-rolled or normalized steels than in annealed steels.

2. As the carbon content of a steel increases, the influence of copper on the strength and hardness decreases. Further study of the influence of copper on the properties of high-carbon steel is needed.

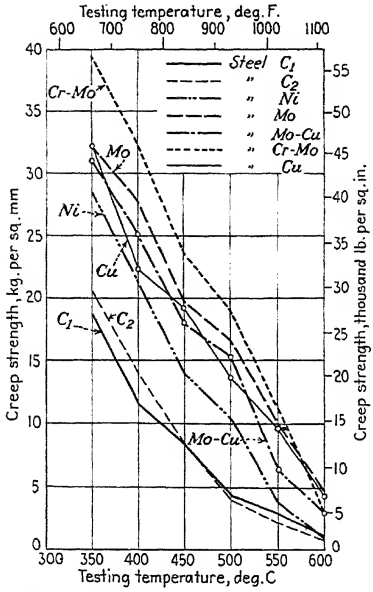


FIG. 109.—Results of accelerated creep tests on steels whose compositions are given in Table 48. Ordinate represents load producing an elongation of 0.003 per cent per hour between the fifth and tenth hour. (*Pomp and Enders.*[331])

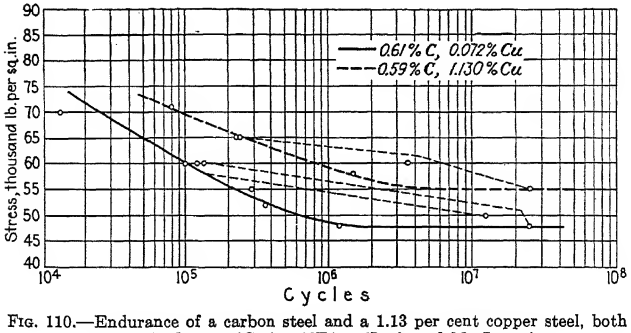


FIG. 110.—Endurance of a carbon steel and a 1.13 per cent copper steel, both normalized at 850°C. (1560°F.). (*Lorig and MacLaren.*)

3. Copper when present up to about 2 per cent has but little influence on the ductility of wrought steel.

4. The most noticeable influence of copper is on the yield strength of steel, this being appreciably increased by the copper, particularly for normalized steels and for steels hardened by precipitation.

5. Normalized and reheated steels containing from 1 to 2 per cent copper are much stronger than carbon steels in a similar condition.

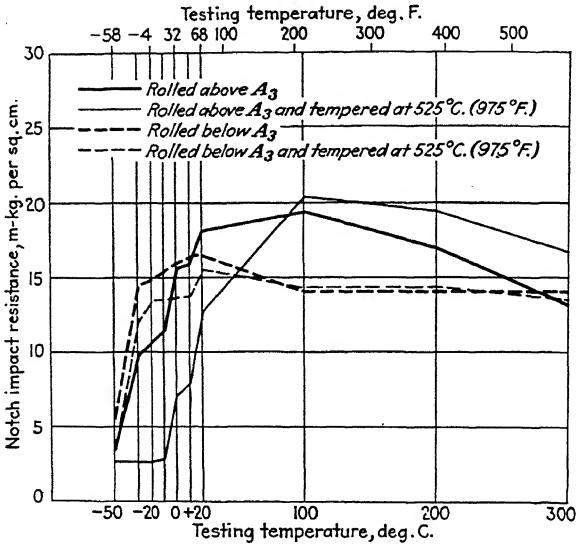


FIG. 111.—Temperature-versus-impact-resistance curves for a copper steel.

6. Copper increases the tensile strength of low-carbon steels at elevated temperatures, at least for temperatures up to 500°C. (930°F.). However, it should be remembered that copper begins to precipitate from ferrite at about 400°C. (750°F.) and that this may cause copper steels to soften slowly when held at temperatures above 400°C. (750°F.).

7. No true creep data on copper steels are available, but the results of accelerated tests indicate that the creep strength may be improved by copper.

8. The endurance limit rises with the tensile strength, which is increased by copper, these two changes being in the same

proportion. The information available indicates that copper has little influence on the resistance of steel to corrosion fatigue.

9. The influence of copper on the aging characteristics of steel is uncertain and deserves further study. Copper alone apparently does not prevent low-temperature impact brittleness. This also should be investigated further.

CHAPTER IX

CORROSION RESISTANCE OF COPPER STEEL AND IRON

Atmospheric Corrosion—Submerged Corrosion—Underground Corrosion—Protective Coatings—Theories—Authors' Summary

The use of copper as an alloying element in steel does not "solve the corrosion problem" or produce a "rustless steel." The order of improvement produced by copper is a relatively small one compared with that obtained by the use of large amounts of chromium in the so-called "stainless steels." Moreover, the improvement in corrosion resistance caused by copper is obtained only under some, but not all, corrosive conditions. Nevertheless, the prolongation of the life of a steel article under atmospheric exposure by approximately 50 per cent and at the slight cost of adding a few tenths of 1 per cent of copper is of marked economic advantage.

That definitely provable extension of the life of steel under atmospheric exposure can be obtained by addition of copper has been acrimoniously disputed by manufacturers of other materials. However, it has now been so thoroughly substantiated that little attention need be paid to the literature of such discussions. That the fact has been accepted by users who are competent to form their own opinions on the basis of test and experiment is evidenced by the following excerpt from McDonnell:[157]

The author's tests of 1913 together with the obvious outcome of the A.S.T.M. Pittsburgh tests led the Pennsylvania [Railroad] management in 1919 to adopt copper-bearing steel for all sheet steel to be used in cars.

A statement has been prepared showing the cost of maintaining car bodies in which the calculations are based on an average length of life for the plain carbon steel, which is 10 years between Class I repairs. The estimates of materials and cost of maintenance for copper-bearing steel cars represent an anticipated 50 per cent greater durability than for the plain-carbon-steel cars, or a 15 year service prior to Class I repairs. No allowance is made for painting the cars or for any repairs to the underframes, trucks, or brake equipment. The increased cost of cars due to the use of copper-bearing steel is shown. This is obtained by applying the differential of $3.00 per ton which has prevailed between

plain carbon and copper-bearing steel plates. This amount may diminish when the amount of copper-bearing scrap now being used by the steel makers is increased. In making the calculation, allowance is made for losses in fabrication caused by shearing and punching. It is shown that the 135,523 cars involved would have cost $2,509,295.86 more if they had been made of copper-bearing steel. The statement shows the amount of new finished plates, shapes, and rivets, as well as the cost of material and labor, including shop expenses required to dismantle and rebuild car bodies. If these cars are given Class I repairs over a period of 10 years using plain carbon steel sheets, the annual cost under present market conditions amounts to approximately $5,069,112.03. From the experimental data at hand to date it may be assumed that with the use of copper-bearing steel the interval between Class I repairs will be extended over a 15 year period, and repairing with copper-bearing steel sheets reduces this cost to approximately $3,473,710.30. This represents an annual saving of $1,595,401.73 and an annual reduction of 22,385 tons in the amount of new steel required.

A. ATMOSPHERIC CORROSION

The great economic importance of the loss of iron and steel by atmospheric corrosion and the realization that small amounts of copper tend to decrease this loss have resulted in many investigations conducted with the object of determining just how effectively copper steels resist atmospheric corrosion.

96. Early Investigations.—Although numerous references to the effects of copper on the physical properties of iron and steel occur in the literature, beginning as far back as 1627, definite information on the corrosion resistance of these materials is confined to the literature of the present century. In 1900, Williams,[36] as a result of some rather limited experiments, concluded that 0.40 per cent copper increased the corrosion resistance of wrought iron and soft steel subjected alternately to the action of air and water.

Copper steel containing 0.15 to 0.30 per cent copper was first marketed in 1911 by the American Sheet and Tin Plate Company[97] and the Newport Rolling Mill Company.* Of course, some of the early ferrous products contained small amounts of adventitious copper; today they would be described as copper-bearing materials.

In 1912, Burgess and Aston,[66] on the basis of tests on specimens exposed for 5.5 months to atmospheric influence, reported that the

* Fleming, private communication.

corrosion rate of iron is reduced by alloying with copper, some 0.20 per cent being sufficient to obtain good results and further addition of copper producing little effect. They also reported that the influence of copper surpasses that of nickel and that no relation was found between the results obtained in the atmospheric and the acid-solution tests. In 1913, Buck[69] reported the results of an extensive series of tests on bare sheet metal under actual service conditions in three different kinds of atmosphere. Sheets, 16 and 27 gage, of basic open-hearth, rephosphorized basic open-hearth, and regular Bessemer steels with nil to 0.35 per cent copper were exposed for about a year. In every case the steels containing from 0.15 to 0.30 per cent copper showed a decided superiority over similar steels without copper.

These conclusions were confirmed by Buck's later work.[78,80,90,97] Tests made on 700 full-sized sheets of 44 different varieties of steel with copper varying from 0.04 to 2.0 per cent indicated that an appreciable effect is evident with as low a copper content as 0.04 per cent, and that the maximum corrosion resistance is reached with 0.25 per cent. Further additions of copper up to 2 per cent are of little benefit. Buck also claimed that the harmful influence of high sulphur is neutralized by 0.25 per cent copper. He noted a better uniformity, tenacity, and adherence of the scale on copper steels as compared with that of copper-free steels.

Richardson and Richardson,[81] from a series of atmospheric tests, concluded that copper-bearing steels are decidedly superior to pure iron, ordinary steel, or charcoal iron, and that copper increases the corrosion resistance of steel more than of iron. These investigators attributed the greater corrosion resistance of steels to the influence of manganese and, therefore, suggested the addition of manganese to commercial pure irons. Their observations were confirmed by Kalmus and Blake,[83] who concluded that the addition of from 0.25 to 0.75 per cent copper to ingot iron reduces the corrosion under atmospheric conditions. Hoyt,[92] from an extensive set of tests, found that copper steels containing from 0.20 to 0.25 per cent copper offer the greatest resistance to corrosion of the common sheeting materials. From a limited number of atmospheric-corrosion tests of 3 months' duration, Hadfield[129] concluded that copper steel (0.27 per cent copper) is more resistant to corrosion than ordinary steel, especially in an industrial atmosphere.

97. Corrosion of Old Wrought Iron and Steel.—Storey[86] examined a number of old fence wires collected from farms in Wisconsin. From their histories and analyses he concluded that the durability of old steel and wrought-iron wires was due to the presence of copper which came from copper-bearing ores of the eastern United States and from imported ores. Richardson and Richardson,[117] from their examination of a large number of pieces of old iron, such as nails, wires, nuts, and bolts, which had been exposed to atmospheric corrosion for as long as 30 years, found that those pieces that had shown marked corrosion resistance contained copper and those that were badly corroded contained none, or very little. Although the results apparently confirmed the conclusions of Storey, it is not certain but that some of the pieces might have been galvanized. Richardson[103,119] believed that the results obtained by many investigators (up to 1921) warranted the conclusion that any of the ordinary varieties of iron with the addition of 0.10 to 0.50 per cent copper are more resistant to atmospheric corrosion than irons without the addition.

The unusual longevity of old wrought iron was illustrated in the following observations.[138,172] Railroad cars built by the Baltimore and Ohio Railroad in 1862 had wrought-iron bodies, and some were found still in existence in 1923. In an old rolling mill at Cumberland, Maryland, some iron stacks have been subjected to the corrosive air of the mill yards from 1870 to 1920 with only slight signs of corrosion. Analyses of samples of these materials indicated that their longevity might be ascribed to copper which was found in amounts of 0.35 to 0.54 per cent.

It may be of interest to note that some of the earlier investigators probably underestimated the effect of copper because of the lack of accurate analyses. Colby[31] found that early analyses for copper frequently were too low owing to faulty methods.

Although the foregoing evidence indicated clearly the beneficial effect of copper on the resistance of steel to atmospheric corrosion, the opinions of various investigators on certain points were still divided. In the literature on the subject is recorded a famous controversy between the two groups; one, headed by Buck,[78,90,97] the Richardsons, and others, was in favor of copper; the other, led by Cushman[98] and Aupperle and Strickland,[108] questioned the conclusions of the first group. This controversy was ended by the results of extensive systematic investigations, particularly

those by the American Society for Testing Materials, by Staatliches Materialprüfungsamt in Germany, and by the Corrosion Committee of the Iron and Steel Industrial Research Council and Institution of Civil Engineers in England.

98. German Atmospheric-corrosion Tests.—The work of Buck aroused considerable interest in Germany. In 1914, the German Institute for Testing Materials decided to conduct an extensive series of atmospheric-corrosion tests on sheets of German manufacture in order to verify the observations of American investigators and particularly to determine whether the copper or any other accompanying element or factor is responsible for increased corrosion resistance.

The corrosion tests, under the direction of Bauer,[109] started in 1914 and lasted from 4 to 4.5 years. Ingots of basic open-hearth steel, basic Bessemer steel, and steel prepared by the pig-ore process were rolled into 1000 × 500-mm. (40 × 20-in.) sheets of 2-mm. (0.078-in.) thickness, corresponding approximately to U. S. Standard 14 gage for sheet and plate steel. Sheets were made from top, middle, and bottom parts of the ingots. The chemical composition varied within the following ranges:

Element	Percentage
Carbon	0.04 to 0.13
Manganese	0.35 to 0.58
Phosphorus	0.012 to 0.097
Sulphur	0.03 to 0.08
Silicon	Trace
Copper	0.07 to 0.46

Most of the steels contained from a trace to 0.01 per cent chromium and between 0.05 and 0.10 per cent nickel.

The sheets, with the scale unremoved, were exposed in three different localities: (1) in a relatively pure (city) atmosphere, (2) in the salt air on the North Sea coast, and (3) in industrial atmosphere at a steel works. Unfortunately, no material free from copper was included in the tests, and the comparisons to determine the effect of copper could only be made on steels in which the copper content varied from about 0.10 to 0.40 per cent. The results of the tests, shown in Fig. 112, were summarized by Bauer as follows:

In clean air and sea-coast air some steels with higher copper content rusted somewhat less than those with lower copper content. On the other hand in some cases the higher copper sheets were attacked more

than the lower copper sheets. These observations and the scatter in the individual results made it impossible to draw any definite conclusion regarding the effect of copper.

A definite indication of the beneficial effect of the increasing copper content was observed only in the tests in the industrial atmosphere. In all cases the steels rich in copper rusted less than those poor in copper.

The results also indicated that the corrosive attack on all steels was the most severe in the industrial atmosphere, intermediate in the marine, and the least in clean atmosphere.

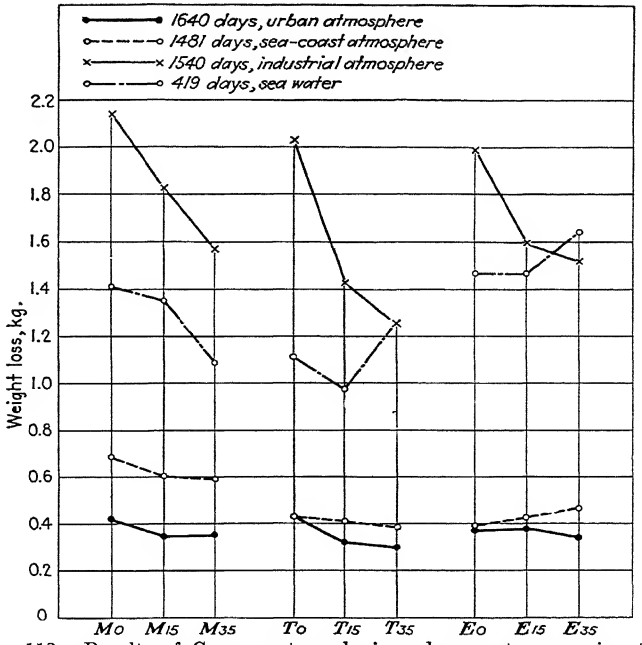


FIG. 112.—Results of German atmospheric and sea-water corrosion tests. (The subscripts 0, 15, and 20 stand for approximately 0.10, 0.20, and 0.40 per cent copper respectively). (*Bauer.*[109])

Briefly, Bauer's conclusion was that copper prolongs the life of steel sheet only in industrial atmosphere containing sulphurous and carbonic acids and has no effect on steels exposed to clean air and to marine atmospheres.

Daeves[163,164,197] studied Bauer's data and interpreted them as indicating the beneficial effect of copper in some cases where

Bauer failed to see any effect. The data, subdivided according to the kinds of steel without regard to the type of atmosphere, indicated that the corrosion was considerably reduced by addition of copper, and that basic Bessemer steel was benefited more than open-hearth steel. Curves plotted by Daeves are shown in Fig. 113.

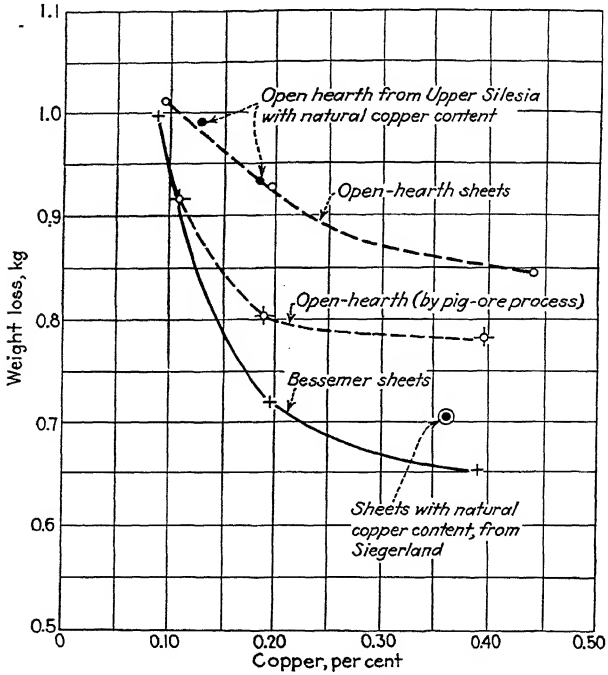


FIG. 113.—Bauer's atmospheric-corrosion data arranged according to kinds of steel. Average loss in weight of six black sheets exposed to different types of atmosphere. (*Daeves.*[163,164])

The relatively small effect of copper in steels in an industrial atmosphere and the failure to observe any effect of copper in steels exposed to other types of atmosphere may be due to the fact that Bauer's tests did not include any copper-free materials, the lowest copper content of the samples being about 0.10 per cent, which is lower than the 0.15 per cent copper of the non-copper steels of the A.S.T.M. tests. Daeves' own tests confirmed the results of other investigators, *viz.*, that 0.25 per cent copper appreciably increases resistance to atmospheric corrosion. From

the study of all available data (1926) he concluded that the life of copper-steel sheets is approximately 50 per cent longer than that of copper-free steel sheets.[164]

Another extensive series of atmospheric tests was conducted in Germany in 1927–1932. Tests were made on three types of basic steel with carbon contents of about 0.10, 0.20, and 0.30 per cent, and the copper varying from 0.03 to 1.07 per cent. A preliminary report[254] based on the results obtained on sheet specimens (0.197 in. thick) exposed to city atmosphere for 3.6 and 9 months indicated that in all cases the corrosion decreased with increase in copper. The minimum corrosion loss was attained with about 0.20 to 0.30 per cent copper, further increase in copper content having little influence on the corrosion rate.

99. A.S.T.M. Atmospheric-corrosion Tests.—These tests were begun in 1916 and were planned on a comprehensive scale. Unprotected corrugated sheets of 22 and 16 gage with scale were exposed in 1916 in three localities representing three different types of atmosphere: (1) Pittsburgh (industrial atmosphere), (2) Fort Sheridan, Illinois (rural), and (3) Annapolis, Maryland (marine atmosphere). The following types of materials supplied by various steel companies were included in the tests:

Low-copper commercially pure iron.
Copper-bearing commercially pure iron.
Low-copper wrought iron.
Copper-bearing wrought iron.
Copper-bearing Bessemer steel.
Low-copper Bessemer steel.
Low-carbon basic open-hearth steel.
Copper-bearing basic open-hearth steel.
Copper-bearing acid open-hearth steel.

The materials were classified as copper bearing and non-copper bearing, the dividing line being 0.15 per cent copper. The highest copper content was 0.60 per cent. Annual inspections were made, and the condition of the sheets and the number of failures were reported. These reports are published in the *Proceedings* of the American Society for Testing Materials from 1916 to date.

The tests in the *industrial atmosphere* (Pittsburgh) were concluded in 1923, after 6.5 years' exposure. In the 16-gage series none of the 132 copper-bearing iron and steel sheets failed, while

TABLE 51.—RESULTS OF PITTSBURGH TESTS. COMPARISON OF COPPER-BEARING AND NON-COPPER-BEARING MATERIALS*

Designation by steel manufacturer†	Description by A.S.T.M.	Average analysis, per cent						Number of sheets in test	Number of sheets failed in test
		C	Mn	P	S	Si	Cu		
No. 16 gage sheets									
Puddled iron	Copper-bearing	0.035	0.03	0.119	0.018	0.125	0.319	12	None
Copper-bearing basic open-hearth steel	Copper-bearing	0.074	0.373	0.011	0.026	0.004	0.237	15	None
Copper-bearing Bessemer steel	Copper-bearing	0.059	0.371	0.095	0.066	0.006	0.247	18	None
Copper-bearing acid open-hearth steel	Copper-bearing	0.108	0.433	0.035	0.043	0.005	0.234	10	None
Copper-bearing pure iron	Copper-bearing	0.023	0.026	0.005	0.028	0.005	0.236	12	None
Copper-bearing steel, Newport Rolling Mill Co	Copper-bearing	0.080	0.313	0.009	0.020	0.006	0.223	14	None
Copper-bearing pure iron, Allegheny Steel Co	Copper-bearing	0.018	0.066	0.008	0.028	0.005	0.239	14	None
Copper-bearing pure iron, Whitaker-Glessner Co	Copper-bearing	0.018	0.046	0.007	0.019	0.004	0.299	13	None
Copper-bearing Bessemer steel, Youngstown Sheet and Tube Co	Copper-bearing	0.08	0.40	0.092	0.037	0.004	0.153	1	None
Copper-bearing Bessemer steel, Youngstown Sheet and Tube Co	Copper-bearing	0.09	0.31	0.088	0.047	.....	0.271	3	None
Copper-bearing Bessemer steel, Youngstown Sheet and Tube Co	Copper-bearing	0.07	0.36	0.085	0.033	.....	0.549	3	None
Copper-bearing open-hearth steel, Youngstown Sheet and Tube Co	Copper-bearing	0.06	0.37	0.054	0.064	.....	0.223	3	None
Copper-bearing open-hearth steel, Youngstown Sheet and Tube Co	Copper-bearing	0.09	0.33	0.032	0.056	0.003	0.575	3	None
Copper-bearing open-hearth steel, Youngstown Sheet and Tube Co	Copper-bearing	0.07	0.40	0.050	0.048	.....	0.364	2	None
Total	.....	.....	.....	.....	.....	.....	.....	132	None
Bessemer steel	Non-copper-bearing	0.043	0.419	0.083	0.042	0.004	0.012	17	All
Open-hearth steel	Non-copper-bearing	0.056	0.349	0.022	0.048	0.037	0.113	17	4
Copper-bearing pure iron	Non-copper-bearing	0.019	0.029	0.004	0.032	0.003	0.067	12	6
Low-copper pure iron	Non-copper-bearing	0.019	0.028	0.004	0.027	0.004	0.028	18	17
Low-copper open-hearth steel	Non-copper-bearing	0.108	0.371	0.009	0.029	0.007	0.029	12	All
Open-hearth steel, Alan Wood Iron and Steel Co	Non-copper-bearing	0.017	0.414	0.010	0.029	0.007	0.057	14	11
Low-copper pure iron, American Rolling Mill Co	Non-copper-bearing	0.017	0.021	0.006	0.021	0.006	0.025	14	All
Low-copper pure iron, Inland Steel Co	Non-copper-bearing	0.021	0.062	0.008	0.030	0.005	0.028	14	All
Low-copper wrought iron, Youngstown Sheet and Tube Co	Non-copper-bearing	0.03	0.051	0.123	0.019	0.203	0.023	3	All
Bessemer steel, Youngstown Sheet and Tube Co	Non-copper-bearing	0.07	0.40	0.097	0.037	0.008	0.013	3	All
Open-hearth steel, Youngstown Sheet and Tube Co	Non-copper-bearing	0.032	0.40	0.044	0.028	.....	0.028	2	1
Total	.....	.....	.....	.....	.....	.....	.....	126	102
No. 22 gage sheets									
Open-hearth steel	Copper-bearing	0.06	0.27	0.014	0.053	0.006	0.179	9	All
Copper-bearing pure iron	Copper-bearing	0.015	0.028	0.006	0.036	0.003	0.190	9	All

TABLE 51.—RESULTS OF PITTSBURGH TESTS. COMPARISON OF COPPER-BEARING AND NON-COPPER-BEARING MATERIALS.*
(*Continued*)

Designation by steel manufacturer†	Description by A.S.T.M.	Average analysis, per cent						Number of sheets in test	Number of sheets failed in test
		C	Mn	P	S	Si	Cu		
Puddled iron	Copper-bearing	0.033	0.034	0.114	0.021	0.134	0.283	12	All
Copper-bearing basic open-hearth steel	Copper-bearing	0.069	0.387	0.016	0.027	0.004	0.244	12	All
Copper-bearing Bessemer steel	Copper-bearing	0.041	0.365	0.097	0.068	0.008	0.252	18	None
Copper-bearing acid open-hearth steel	Copper-bearing	0.107	0.447	0.091	0.046	0.004	0.237	16	11
Open-hearth steel, Alan Wood Iron and Steel Co	Copper-bearing	0.093	0.419	0.013	0.041	0.011	0.185	14	All
Copper-bearing steel, Newport Rolling Mill Co	Copper-bearing	0.083	0.313	0.009	0.020	0.005	0.227	14	All
Copper-bearing pure iron, Allegheny Steel Co	Copper-bearing	0.017	0.074	0.008	0.037	0.005	0.260	14	All
Copper-bearing pure iron, Whitaker-Glessner Co	Copper-bearing	0.018	0.051	0.007	0.021	0.005	0.304	14	All
Copper-bearing Bessemer steel, Youngstown Sheet and Tube Co	Copper-bearing	0.039	0.37	0.084	0.038	0.007	0.257	3	All
Copper-bearing Bessemer steel, Youngstown Sheet and Tube Co	Copper-bearing	0.043	0.37	0.100	0.045	.....	0.533	2	All
Copper-bearing open-hearth steel, Youngstown Sheet and Tube Co	Copper-bearing	0.06	0.35	0.049	0.059	.....	0.212	3	All
Copper-bearing open-hearth steel, Youngstown Sheet and Tube Co	Copper-bearing	0.07	0.39	0.059	0.058	.....	0.268	3	All
Copper-bearing open-hearth steel, Youngstown Sheet and Tube Co	Copper-bearing	0.07	0.41	0.050	0.050	.....	0.621	3	All
Total	.....	.....	.....	.....	.....	.....	.....	146	123
Bessemer steel	Non-copper-bearing	0.038	0.386	0.089	0.040	0.007	0.014	17	All
Open-hearth steel	Non-copper-bearing	0.09	0.38	0.017	0.062	0.030	0.082	4	All
Copper-bearing pure iron	Non-copper-bearing	0.01	0.028	0.002	0.027	0.002	0.139	2	All
Low-copper pure iron	Non-copper-bearing	0.02	0.020	0.004	0.022	0.002	0.024	9	All
Low-copper open-hearth steel	Non-copper-bearing	0.121	0.536	0.008	0.030	0.249	0.020	12	All
Low-copper pure iron, American Rolling Mill Co	Non-copper-bearing	0.02	0.023	0.006	0.022	0.004	0.022	14	All
Low-copper pure iron, Inland Steel Co	Non-copper-bearing	0.021	0.055	0.007	0.031	0.004	0.027	14	All
Low-copper wrought iron, Youngstown Sheet and Tube Co	Non-copper-bearing	0.03	0.055	0.139	0.021	0.218	0.020	3	All
Bessemer steel, Youngstown Sheet and Tube Co	Non-copper-bearing	0.055	0.37	0.119	0.048	0.003	0.013	3	All
Bessemer steel, Youngstown Sheet and Tube Co	Non-copper-bearing	0.07	0.40	0.088	0.048	0.009	0.133	3	All
Open-hearth steel, Youngstown Sheet and Tube Co	Non-copper-bearing	0.10	0.32	0.069	0.044	0.002	0.018	3	All
Total	.....	.....	.....	.....	.....	.....	.....	84	84

* *Proc. A.S.T.M.*, vol. 23, part I, Table II, Plate II, between pp. 150–151, 1923.

† Material designated as "pure iron" is commercially pure ingot iron. Materials designated by manufacturer as "steel" or "open-hearth steel" without qualifying adjective are probably "basic."

TABLE 52.—RELATIVE ATMOSPHERIC CORROSION OF BLACK UNCOATED SHEETS IN AN INDUSTRIAL DISTRICT—AVERAGE RESULTS OF PITTSBURGH TESTS, AMERICAN SOCIETY FOR TESTING MATERIALS*

Material	Copper under 0.03 per cent		Copper between 0.03 and 0.15 per cent		Copper over 0.15 per cent	
	Number of sheets	Life, months	Number of sheets	Life, months	Number of sheets	Life, months
22 gage						
Open-hearth steel	15	17.2	4	31.5	74	54.5(5)†
Bessemer steel	20	16.9	3	64.0	23	73.7(18)
Average for steel	35	17.0	7	45.4	97	59.1(23)
Open-hearth pure iron	37	22.8	2	38.0	37	43.8
Wrought iron	3	28.0	..	.....	12	31.5‡
16 gage						
Open-hearth steel	14	58.4(1)	31	69.7(16)	56	75.0(56)
Bessemer steel	20	30.5	..	.....	25	75.0(25)
Average for steel	34	41.9(1)	31	69.7(16)	81	75.0(81)
Open-hearth pure iron	46	52.0(1)	12	70.5(6)	39	75.0(39)
Wrought iron	3	54.0			12	75.0(21)

* Speller.[172]

† Figures in parentheses represent number of sheets which had not failed after 75 months when the test was discontinued.

‡ This group was cracked in corrugation and was perforated at such points, although at other places the surface was apparently in a condition similar to the copper-steel sheets.

in the non-copper-bearing series 102 sheets failed (either by perforating or by forming ragged edges) out of the total of 126. In the 22-gage series all of the 84 non-copper-bearing sheets failed, and with the exception of a few Bessemer steel sheets all of them failed in 3.5 years. Of the copper-bearing steels 123 failed out of 146 sheets, in 6.5 years.

Of the 24 unfailed sheets in the 16-gage series, 7 (out of 58 included in the tests) were commercially pure irons, and 17 (out of 45) were open-hearth steel. In the 22-gage series 18 out of the 23 unfailed sheets were Bessemer (out of 23), and the other 5 (out of 74) were of open-hearth steel. This is in line with the observation of Daeves regarding the superior corrosion resistance of

Bessemer over open-hearth steel; the Bessemer steels used by Daeves were, however, made by the basic process.

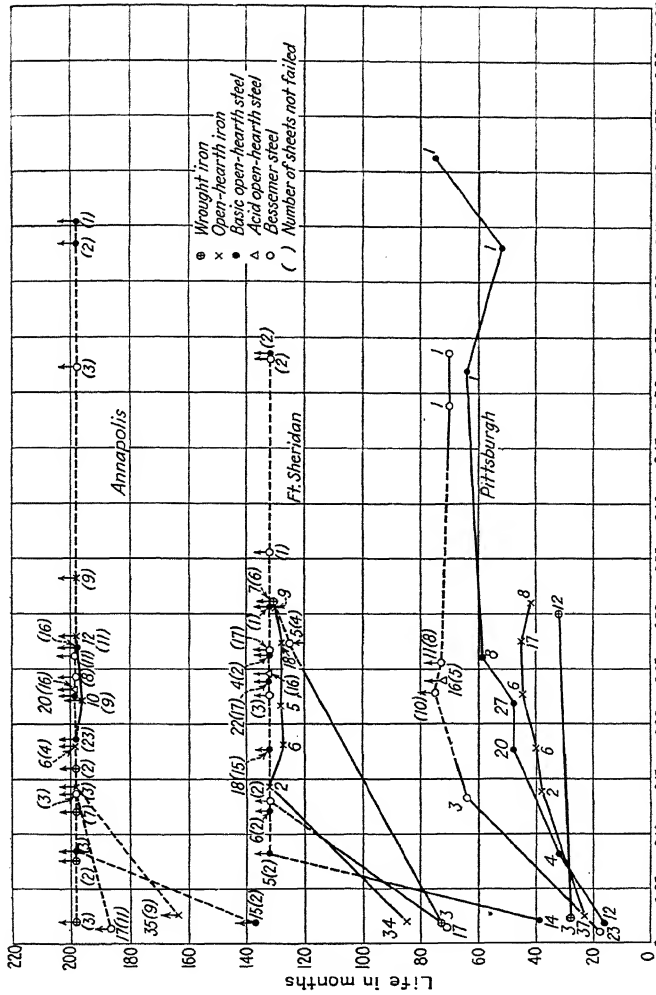


FIG. 114.—Summary of A.S.T.M. atmospheric-corrosion tests on sheet, showing effect of copper. (*Speller.*)

The summary at top of page 232 gives the A.S.T.M. rating of the materials, the most resistant coming first.

The number of failures for each material at the completion of the tests and the chemical compositions are given in Table 51.

Rating	
	22 gage
First	Copper-bearing Bessemer steel
Second	Copper-bearing acid open-hearth steel
Third	Copper-bearing basic open-hearth steel
Fourth	Copper-bearing pure iron
Fifth	Copper-bearing wrought iron
Sixth	Low-copper wrought iron
Seventh	Low-copper pure iron
Eighth	Low-copper basic open-hearth steel
Ninth	Low-copper Bessemer steel
	16 gage
First	All copper-bearing materials
Second	Low-copper basic open-hearth steel
Third	Low-copper pure iron
Fourth	Low-copper Bessemer steel

In Table 52, compiled by Speller,[172] is given the average life for sheets classified according to copper content.

Figure 114 was prepared for a new edition of Speller's book and he has kindly allowed it to be reproduced here. The figure summarizes the A.S.T.M. results and shows quite strikingly how copper increases the resistance to atmospheric corrosion.

The tests in *rural atmosphere* were discontinued in 1928, after 11 years' exposure. In the 16-gage series none of the 136 copper-bearing sheets failed and only 4 of the 124 non-copper-bearing sheets (4 out of the 12 Bessemer sheets). In the 22-gage series 50 of the 136 copper-bearing and 77 of the 83 non-copper-bearing sheets failed. The total failures were distributed among the different groups of materials as follows:

Material	Total number of sheets exposed	Number of failures
Copper-bearing pure iron	38	38
Copper-bearing wrought iron	12	2
Copper-bearing open-hearth steel	63	10
Copper-bearing Bessemer steel	23	0
Total in copper-bearing material	136	50
Non-copper-bearing pure iron	36	36
Non-copper-bearing wrought iron	3	3
Non-copper-bearing open-hearth steel	25	21
Non-copper-bearing Bessemer steel	19	17
Total in non-copper-bearing material	83	77

The beneficial effect of copper is at once apparent from this table. The order of resistance determined by the society on the basis of these tests is shown below, the most resistant materials coming first.

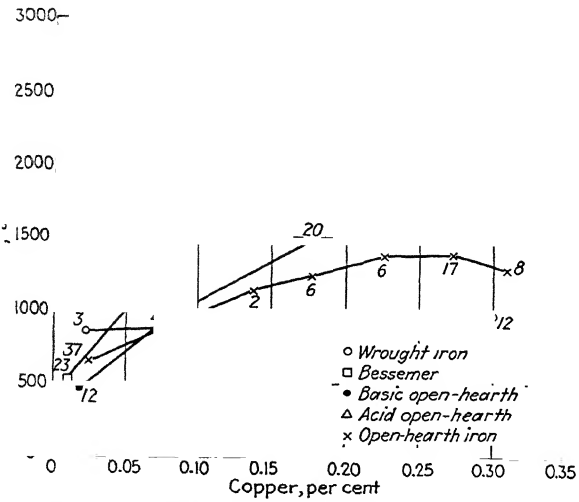
Rating	Type of Material
First	Copper-bearing open-hearth and Bessemer steels
Second	Copper-bearing wrought iron and copper-bearing open-hearth steels
Third	Copper-bearing pure iron
Fourth	Non-copper-bearing pure iron
Fifth	Non-copper-bearing wrought iron
Sixth	Non-copper-bearing Bessemer steel
Seventh	Non-copper-bearing open-hearth steel

As may be seen by comparing the table with that for the Pittsburgh tests, the order of the various materials is substantially the same. The difference between the two series of tests is in the life of sheets, which is considerably longer in the rural than in the industrial atmosphere, as may be seen from comparison of Figs. 115 and 116, from Kendall and Taylerson.[236]

The tests in *marine atmosphere* (Annapolis) are still being continued (1933). The sheets have stood remarkably well in comparison with those at Pittsburgh and Fort Sheridan locations. At the end of an exposure of 17 years none of the 16-gage sheets had failed, and only 48 of the total of 227 sheets (148 copper-bearing plus 79 non-copper-bearing) in the 22-gage series had failed. Of these 48 failed sheets only 4 were copper-bearing materials. The failures are tabulated below according to the types of materials:

Material	Total number of sheets exposed	Number of failures
Copper-bearing pure iron	37	4
Copper-bearing other materials	111	0
Total in copper-bearing material	148	4
Non-copper-bearing open-hearth steel	18	12
Low-copper pure iron	38	26
Non-copper-bearing Bessemer steel	20	6
Non-copper-bearing wrought iron	3	0
Total in non-copper-bearing material	79	44

The superiority of copper-bearing materials is again demonstrated; in the copper-bearing group only 4 failed out of a total of 148 sheets, while in the non-copper-bearing series 44 failed



G. 115.—Relation of average life of sheets to copper content. Pittsburgh tests, 22-gage sheets. (*Kendall and Taylerson.*[236])

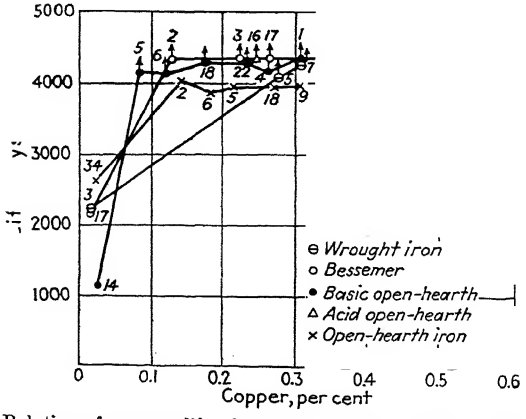


FIG. 116.—Relation of average life of sheets to copper content. Fort Sheridan tests, 22-gage sheets. (*Kendall and T*

out of the total number of 79 sheets. Since the tests have not yet been completed, no rating of the materials has yet been published.

TABLE 53.—SUMMARIZED RESULTS OF THE A.S.T.M. ATMOSPHERIC-CORROSION TESTS*

Location of test	Duration of test		Material			Failures to date	
	Begun	Finished	Gage	Kind	Number of sheets	Number	Percentage
Pittsburgh, Pa. (industrial)	Dec., 1916	March, 1923	No. 22	Copper	146	123	84.4
				Non-copper	84	84	100.0
				Total	230	207	90.0
			No. 16	Copper	132	None	0.0
				Non-copper	126	102	81.0
				Total	258	102	39.5
Fort Sheridan, Ill. (rural)	Apr., 1917	Apr., 1928	No. 22	Copper	136	50	36.8
				Non-copper	83	77	92.8
				Total	219	127	58.0
			No. 16	Copper	136	None	0.0
				Non-copper	124	4	3.2
				Total	260	4	1.5
Annapolis, Md. (marine)	Oct., 1916	Last inspection Apr., 1933	No. 22	Copper	148	4	2.7
				Non-copper	79	44	55.7
				Total	227	48	21.1
			No. 16	Copper	130	None	0.0
				Non-copper	129	None	0.0
				Total	259	None	0.0

* Kendall and Taylerson,[236] revised.

Annual inspections showed that the sheets which failed first at the Annapolis location belonged to the same group of low-copper open-hearth steel and low-copper pure iron that failed first at the Pittsburgh and Fort Sheridan tests. This indicates that the three different atmospheric conditions show the same general tendencies, only with varying rates of corrosion.

100. Summary of A.S.T.M. Atmospheric-corrosion Tests.—Summarized results of the A.S.T.M. atmospheric tests are given in Table 53, compiled by Kendall and Taylerson,[236] and are brought up to date (1933) by including additional data obtained on Annapolis tests for the 5 years from 1928 to 1933.

Recent papers by Hocker[393] and Passano[398] discuss the significance of the A.S.T.M. tests on atmospheric corrosion and analyze the data reported.

101. Atmospheric-corrosion Tests by the Institution of Civil Engineers (British).—These tests were initiated in 1916 and are still being continued.[128,133,155,205,235] Specimens were exposed at Plymouth, England; Halifax, Nova Scotia; Auckland, New Zealand; and Colombo, Ceylon to "aerial" (atmospheric), alternate-wet-and-dry, and complete-immersion corrosion. Five types of specimens in each of a great variety of materials were used. The aerial tests were made on rectangular bars, 24 × 3 × 0.5 in., which were exposed to sea air and salt-water spray.

The results of tests (1929) have clearly indicated a decided beneficial effect of copper on mild steel—as may be seen by comparing steels *G* and *H* with steel

Bar	Copper, per cent	Weight loss, g. per sq. cm.	Reduction in thickness, per cent	Deepest pits, mm.	
				Front	Back
F	0.09	1.496	19.7	4.56	1.18
G	0.63	1.379	12.7	1.77	1.17
H	2.18	1.204	15.3	1.31	1.24

Inspection made in 1933[353] confirmed the foregoing results but showed that the superiority of copper steels becomes less pronounced as the corrosion is allowed to continue.

102. Atmospheric-corrosion Tests by the (British) Iron and Steel Institute.—These tests were begun in 1931. The investigation is planned on a very comprehensive scale, and the work in

progress includes (1) tests on the corrosion of ordinary mild steel with and without the addition of small amounts of copper, (2) tests on the corrosion of wrought iron and ingot iron, and (3) tests on the possible effects of differences in the process of manufacture on the corrosion of iron and steel. The reader is referred to the first *Report* of the Corrosion Committee to the Iron and Steel Industrial Research Council, published in 1931 by the British Iron and Steel Institute.[281] To date* no results regarding the effect of copper have been obtained, but the report contains a great deal of valuable information on corrosion of copper steel, preparation of steels for tests, analyses, etc.

103. Other Investigations.—Speller[172] made a series of tests on soft steel strips which were exposed to industrial atmosphere for over 6 years in the mill yards of the National Tube Company near Pittsburgh. These tests confirmed the previous results as to the beneficial effect of copper. Further tests were made by suspending short lengths of wrought iron, steel, and copper-bearing steel in the vent lines of large buildings in New York City and Chicago. The average results obtained by measuring the deepest pit in each piece of material exposed in several places in each locality are given below:

Tests	Average maximum penetration, in. per year		
	Wrought iron	Steel	Copper steels
4-year tests, New York City....	0.0132	0.0189	0.0055
2-year tests, Chicago.....	0.0231	0.0215	0.0084

Further tests were made by the National Tube Company[223] in which short lengths of black pipe 1 in. in diameter were exposed to Pittsburgh atmosphere for over 9 years. The results are given below:

Copper, per cent....	Nil	0.056	0.129	0.216
Loss in weight per ft.	0.778	0.225	0.171	0.192

* The second report was published in 1934. It shows that 2 years' atmospheric exposure of wire indicated that the loss in strength of wires containing 0.2 and 0.5 per cent copper was less than for wire containing no copper. Results of other tests on copper-bearing steels were inconclusive owing to the comparatively short time of exposure of the samples to the atmosphere.

Telegraph wires of copper steels were found by Greger and Virgin[351] to be more resistant to atmospheric corrosion than copper-free materials.

Van Royen and coworkers[301] reported tests to prove that copper steels were more resistant than copper-free steels when exposed to steel-mill atmospheres.

Exposure tests of copper-bearing steels made in various countries have been recently summarized by Hudson.[394] He stated that Dr. Greger of the Statens Provningsanstalt, Stockholm, Sweden, studied 3-mm. diameter wires of various irons and low-carbon steels for telegraph conductors, exposed by stringing on telegraph poles in three parts of Sweden. Corrosion was evaluated by the increase in electric resistance of the wires. Hudson says, "once again, two copper-bearing materials head the list in corrosion resistance." These were a 0.30 per cent copper basic open-hearth steel and a 0.15 per cent copper electric steel.

104. Atmospheric-corrosion Tests of Railroad Materials.—Considerable work has been done by various railroad companies to determine the effect of copper on the life of iron and steel used in various types of railroad equipment. Since the results were favorable, many companies adopted copper steel for railroad cars, tie-plates, structural and other material.

Neubert[100] described tests made by the New York Central Railroad. The tests were made on tie-plates with copper varying from 0.25 to 0.50 per cent. The exposure varied from 2 to 6 years. In all cases the maximum corrosion developed on the underside of the plates, but the weight loss of the copper-free steels was on an average eight to ten times greater than that of the copper steels.

Marzahn and Pusch[298] subjected plates of various steels to the influence of corrosive locomotive smoke in a vertex of a tunnel where the gases accumulate. The corrosion resistance of the black plates and the scale-free plates was considerably improved by the addition of copper. In another paper[297] Marzahn suggested the use of copper-steel rails in tunnels.

Wolf and Meisse[308] found that the addition of copper to malleable cast iron decreased attack by locomotive smoke. The irons contained as much as 2 per cent copper and were exposed in the smoke jacks of a round-house for 2 years. The samples containing 1 per cent copper were more resistant than those containing 0.25 per cent copper, but raising the copper

content from 1 to 2 per cent had little influence on the corrosion loss.

Service tests of carbon- and copper-steel railroad ties made by the Carnegie Steel Company were described by Unger.[306] The copper steel contained 0.25 per cent copper, the amount of other elements being practically identical in both steels. Seven hundred ties made of each steel were laid, with ashes used as ballast. Inspection made after a few months showed top flanges of copper-steel ties to be smoother, less deeply pitted, and freer from rust than the plain steel ties. On digging away the ballast no great difference was observed, and both types of steel seemed to be pitted to the same extent on the web and base, but there was a heavier coating of rust on the plain steel ties. After 4 years' exposure the plain steel ties were found to have lost in weight from 2 to 3.5 times as much as those of copper steel. After 9 years they were found to be more unevenly pitted than the copper steels. Plain steel ties bent much more than and lost more than twice as much weight as the copper steels.

The Bessemer and Lake Erie Railroad,[123,220] in 1914, ordered 100 gondola cars and 100 hoppers using both copper-bearing and plain steel plates in the same car body. After 6 years' service the copper steel was in a much better condition than the ordinary steel. On the inside of the cars the copper steel was freer from adhering oxide and scale and less deeply pitted than the ordinary steel. It was observed that paint adhered better to copper steel than to plain steel. Where paint had come off on the outside of the car, the surface of the copper steel was smoother. After 13 years' service the average loss in weight due to corrosion was 57 per cent for plain steel and 32 per cent for copper steels.

Several other examples confirming the foregoing observations are given in the *Report* of the Corrosion Committee of the Iron and Steel Institute.[281]

According to Allen,[340] a rail steel containing up to 0.6 per cent copper is recommended in Italy for use in tunnels.

105. Oxidation of Iron-copper Alloys at High Temperatures.—High-temperature oxidation tests by Schenck and coworkers[247] showed that iron containing from 0.5 to 4.0 per cent copper is somewhat nobler than unalloyed iron. The influence of copper on the oxidizability of pure iron-copper alloys at elevated temperatures was studied by Kirscht.[292] He heated the specimens to test temperatures, passed in carbon dioxide gas, and observed

the amount of oxygen the alloy absorbed by analyzing the gas when the equilibrium between CO and CO_2 was reached. The results are shown in Table 54, where the increase in CO_2 content of the gas mixture indicates decreased oxidation of the alloy.

TABLE 54.—INFLUENCE OF SMALL AMOUNTS OF COPPER, NICKEL, AND COBALT ON THE PROCESS OF OXIDATION OF IRON*

Composition	Per cent CO_2 in gas mixture at temperatures given		
	700°C. (1290°F.)	800°C. (1470°F.)	900°C. (1650°F.)
Pure iron.	40.2	34.8	31.2
99.9% Fe, 0.1% Cu...	40.8		
99.75% Fe, 0.25% Cu.	41.2		
99.5% Fe, 0.5% Cu...	41.2	35.8	32.1
99.0% Fe, 1.0% Cu...	40.9		
96.0% Fe, 4.0% Cu...	40.6		
95.5% Fe, 0.5% Ni.		35.	
95.5% Fe, 0.5% Co.		35.	
96.0% Fe, 4.0% Ni.	41.3		

* Kirscht.[292]

It may be seen from the table that copper renders iron very slightly more resistant to oxidation at high temperatures, the greatest effect being attained at 0.25 to 0.5 per cent copper. These tests also indicated that the effect of 0.5 per cent copper, nickel, or cobalt on the equilibrium at 800°C. (1470°F.) is the same.

It has been claimed that copper improves the resistance of iron and steel to corrosive action of products of combustion, such as hot flue gases. Some of the results[122] on which this claim was based are shown at top of page 241.

It was claimed that, since copper reduces the oxidation at high temperatures and the thickness of the scale, the use of copper steel for boiler tubes would be desirable from a heat-transmission standpoint.[147] Actually, the Rock Island Railway uses copper steel for boiler tubes.

Egloff and Morrell[178] reported some results of a corrosion test covering a period of 20 days while cracking 17,000 bl. of California oil containing 1 per cent sulphur at a temperature of 460°C.

Material	Composition, per cent					Average loss, grams per equal areas
	C	Mn			Cu	
Ingot iron	0.02	0.05	0.030	0.008	0.06	37.98
Ingot iron	0.05	0.05	0.036	0.004	0.07	39.52
Copper steel.	0.12	0.42	0.041	0.063	0.24	26.10
	0.10	0.47	0.043	0.018	0.572	20.75
	0.11	0.45	0.032	0.010	0.95	14.41
	0.12	0.46	0.047	0.014	1.118	13.56

(860°F.). Various metals and alloys were suspended in the vapor zone of the reaction chamber, and their loss in weight was observed. Copper-bearing steel lost more than plain steel and hence did not show promise for this particular service.

106. Amount of Copper Necessary to Produce Maximum Resistance to Atmospheric Corrosion.—A careful examination of the data presented above, particularly Tables 50 and 51 and Figs. 115 and 116, indicates that the resistance to corrosion increases rapidly as the copper content increases to 0.25 per cent; further increase in copper content has little influence on the rate of corrosion. The results of various investigations compiled by Daeves[164] are given in Fig. 117, where the comparison is made by assigning the value of 100 per cent corrosion loss to a steel containing 0.10 per cent copper.

B. SUBMERGED CORROSION

While it has been definitely established that copper increases the durability of iron and steel exposed to the atmosphere, the results of underwater-corrosion tests are not in good agreement, particularly for sea-water tests. In general, the influence of copper is considerably weaker than in the atmospheric tests, and the scatter of individual results in both directions apparently may be influenced by the external test conditions in such a way as to deflect the conclusion to one or the other side, *i.e.*, to condemn copper as a harmful element, or to claim for it beneficial effects.

107. A.S.T.M. Total-immersion Tests in Mine, City, and River Water.—The tests were begun in 1920. Portions of the

same sheets that were used in the atmospheric tests were immersed in three types of water: (1) acid mine water at a coal mine near Calumet, Pennsylvania, (2) running city water at the Bureau of Standards, Washington, D. C., and (3) the brackish water of the Severn River, Annapolis, Maryland, where the salinity is from one-fourth to one-third of normal ocean water.

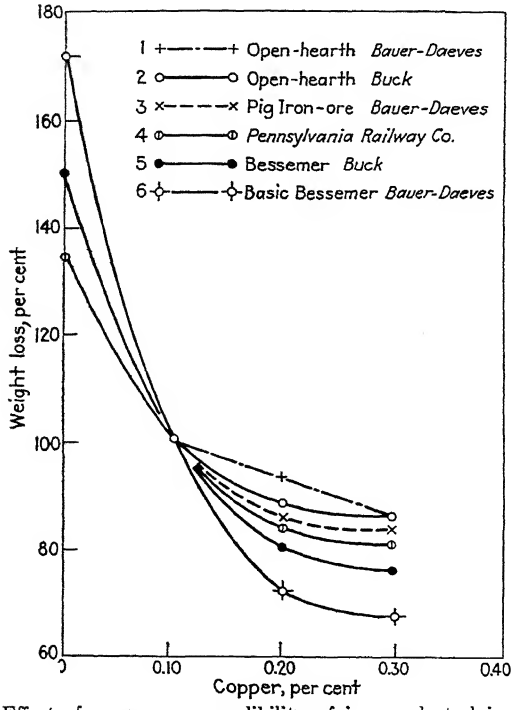


FIG. 117.—Effect of copper on corrodibility of iron and steel in atmosphere.

The specimens were 6 × 2 in. and were the same in number as for the atmospheric tests. They were mounted in boxes, and water was run continuously through the boxes. The flow of water was regulated and the water analyzed monthly for acidity or alkalinity and for oxygen content.

The *mine-water* tests were completed in 167 days. The average life of the sheets as computed by the A.S.T.M. was as shown in Table 55.

TABLE 55.—AVERAGE LIFE OF IRON AND STEEL SHEETS IN MINE WATER*

Material	Average life, days	
	22 gage	16 gage
Bessemer steel, non-copper-bearing	56	135
Bessemer steel, copper-bearing	48	124
Basic open-hearth steel, non-copper-bearing	40	114
Basic open-hearth steel, copper-bearing	46	113
Pure iron, non-copper-bearing	47	124
Pure iron, copper-bearing	45	99
Acid open-hearth steel, copper-bearing	16	109
Wrought iron, non-copper-bearing	47	158
Wrought iron, copper-bearing	50	128

It will be noted that the results are quite different from those obtained in atmospheric tests on the same materials. The average life in the mine water was very short, and the presence of copper had very little effect on the life of the materials.

The *city-water* immersion tests (Washington, D. C.) were completed in 1924 for the 22-gage series and in 1928 for 16-gage sheets.[140,196] The final summary is given in Table 56.

TABLE 56.—AVERAGE LIFE OF IRON AND STEEL SHEETS IMMERSED IN CITY WATER*

Material	Average life, days	
	22 gage	16 gage
Bessemer steel, non-copper-bearing	899	1933
Bessemer steel, copper-bearing	880	1858
Basic open-hearth steel, non-copper-bearing	875	1908
Basic open-hearth steel, copper-bearing	864	1963
Pure iron, non-copper-bearing	900	2049
Pure iron, copper-bearing	968	2074
Acid open-hearth steel, non-copper-bearing	822	1858
Puddled iron, non-copper-bearing	740	1747
Puddled iron, copper-bearing	791	2028

* A.S.T.M.[196]

The results indicate that the average life in city water is fifteen to twenty times longer than in the mine water. The 16-gage sheets (which are double the thickness of the 22-gage sheets)

lasted a little more than twice as long as the thinner gage sheets. Copper in the amounts present again had no appreciable influence on the durability of iron and steel.

The tests in brackish *river water* (Annapolis) were completed in 1926 for the lighter gage and in 1930 for the heavier gage sheets,[162,259] the duration of tests being 6 and 10 years respectively. The summarized results are given in Table 57.

TABLE 57.—AVERAGE LIFE OF IRON AND STEEL SHEETS IMMERSED IN BRACKISH RIVER WATER*

Material	Average life, days	
	22 gage	16 gage
Bessemer steel, non-copper-bearing	1308	2400
Bessemer steel, copper-bearing	1425	2316
Basic open-hearth steel, non-copper-bearing	1342	2120
Basic open-hearth steel, copper-bearing	1343	2469
Pure iron, non-copper-bearing	1269	2005
Pure iron, copper-bearing	1312	1970
Acid open-hearth steel, copper-bearing	1421	2015
Puddled iron, non-copper-bearing	1105	1934
Puddled iron, copper-bearing	1728	2794

* A.S.T.M.[162,259]

The A.S.T.M. Committee reached the same conclusion as on mine- and city-water tests, *viz.*, that there is *no material difference* in corrosion resistance between the copper-bearing and non-copper-bearing metals.

The average life of all materials was considerably longer in brackish river water (Annapolis) than in city water (Washington). According to the A.S.T.M. Committee,[196] this may be explained by the differences in the analyses of the two waters: (1) The river water contains more silica, which may form a more protective scale; and (2) the average oxygen content and the temperatures are lower in the Severn River water.

In Table 58 is given the average life of all the materials in the three different types of water obtained from the actual data by three independent calculations: (1) average life, A.S.T.M., (2) average life computed by Kendall and Taylerson[236] by plotting probability curves, and (3) most probable life computed by Passano and Hayes[241] from probability curves. The rounded average of the three is also given.

TABLE 58.—AVERAGE LIFE OF SHEETS IN MINE, CITY, AND RIVER WATER*

Type of water	Average life, days							
	22 gage				16 gage			
	A.S.T.M.	Kendall and Taylerson	Passano and Hayes	Average	A.S.T.M.	Kendall and Taylerson	Passano and Hayes	Average
Calumet mine water.....	44	48	43	45	121	125	112	119
Washington tap water...	860	880	855	865	1935	1930	1920	1930
Severn River water.....	1360	1300	1295	1320	2225	2200	1920	2115

* Averages of Kendall and Taylerson[236] and Passano and Hayes[241] are from calculations based on data from the American Society for Testing Materials.

108. A.S.T.M. Total-immersion Tests in Sea Water.—In 1926–1927 the A.S.T.M. program was extended to include tests of sheets, riveted plates, and pipes in *sea water*. The sheet samples, cut from the same sheets as in the foregoing series of tests, were immersed in running sea water at the U. S. Naval Station at Key West, Florida, and at the U. S. Navy Yard at Portsmouth, New Hampshire. A 12-in. length of 2-in. pipe of low-copper and a 1 per cent copper steel were also tested at the same locations. A set of riveted ship-plate specimens, a set of three 30-in. lengths of 2-in. tubes of 0.1 to 0.2 per cent carbon steel containing nil to 1.0 per cent copper, and a set of 3-in. tubes of 0.3 to 0.4 per cent carbon steel with copper varying from 0.25 to 1.1 per cent were tested in the same locations and also in the Gulf water at Port Arthur, Texas. In all three locations a series of riveted ship plates was installed to determine the effect of sea-water corrosion on plates riveted with rivets of different analyses. The series of plate specimens ($26 \times 16 \times 0.5$ in.) consisted of three kinds of steel ship plate: (1) 0.04 per cent copper, (2) 0.23 per cent copper, and (3) 0.19 per cent silicon. In each set the two plates were riveted together with four rows of different kinds of rivets: 0.07 per cent copper steel, 0.27 per cent copper steel, 0.02 per cent copper puddled iron, and standard ship quality steel. At Key West and Portsmouth the plates were totally immersed below the low tide to insure against

excessive wave action; at Port Arthur they were placed 9 in. below low mean Gulf level in a channel 9 miles away from the Gulf and subjected to usual tide variations. The proportions of sea and fresh water in the channel vary considerably according to the wet and dry seasons.

To date (1933) only the tests on 22-gage sheets have been completed. In the other tests the corrosion has not proceeded sufficiently far to allow any definite conclusions. Examination of the riveted plates showed pitting and spongy corrosion about equally divided among the various sorts of plates and rivets.

In the heavier gage series, after 6 years' exposure 35 sheets out of 138 failed at Key West and 30 out of 138 at Portsmouth. The average life of the lighter (22-gage) sheets is given in Table 59.

TABLE 59.—AVERAGE LIFE OF IRON AND STEEL SHEETS IMMERSED IN SEA WATER (22 GAGE)*

Material	Average life, days	
	Key West, Fla.	Portsmouth, N. H.
Bessemer steel, non-copper-bearing	733	1134
Bessemer steel, copper-bearing	878	1152
Basic open-hearth steel, non-copper-bearing	939	881
Basic open-hearth steel, copper-bearing	1082	869
Pure iron, non-copper-bearing	1250	917
Pure iron, copper-bearing	1419	960
Acid open-hearth steel, copper-bearing	782	1218
Wrought iron, non-copper-bearing	605	987
Wrought iron, copper-bearing	937	992

* A.S.T.M.(316,346)

Although no official conclusion was given by the A.S.T.M. Corrosion Committee, it may be inferred from the foregoing data that copper has very little effect on the durability of 22-gage sheets in sea water. Interesting results are to be expected from the tests of riveted plates and pipes. At present (1933) the tests have not progressed sufficiently to warrant any conclusions.

The critical study of the A.S.T.M. immersion-corrosion data made by Kendall and Taylerson(236) led them to the conclusion that variations of the chemical elements, singly or in combination

(including copper) within the range of composition studied and under conditions of the tests, have no material influence on the corrosion resistance and are entirely secondary to external conditions, such as oxygen concentration, mill scale, location of test tanks.

TABLE 60.—DESCRIPTION AND CHEMICAL COMPOSITION OF BARS USED IN IMMERSION TESTS AT HALIFAX, COLOMBO, PLYMOUTH, AND AUCKLAND*

Identification mark	Material	Condition	Composition, per cent						
			C	Si	S	P	Mn	Cr	Ni	Cu
	Medium-carbon steel	Cleaned	0.345	0.20	0.025	0.027	0 715			0.076
B	Mild steel	With scale	0.215	0.17	0.103	0.067	0.34			0.072
C	Mild steel	Cleaned	0.24	0.16	0.063	0.048	0 68			0.087
D	Medium-carbon steel	With scale	0.40	0.20	0.049	0.045	0.85			0.048
	Medium-carbon steel	With scale	0.345	0.20	0.025	0.027	0.715			0.076
F	Mild steel	With scale	0.24	0.16	0.063	0.048	0.68			0.087
G	Copper steel	With scale	0.21	0.14	0.043	0.046	0.945			0.635
H	Copper steel	With scale	0.225	0.14	0.034	0.041	0.91			2.185
J	Chromium steel	With scale	0.36	0.22			0.13	13.57		
K	Nickel steel	With scale	0.31	0.18	0.029	0.038	0.54		3.75	
L	36 per cent nickel alloy	With scale	0.12	0.09			0.87		36.55	
M	Armco iron	Cleaned	0.035	0.035	0.033	0.017	0.065			0.042
N	Low Moor wrought iron	Cleaned	0.015	0.145	0.012	0.113	0.02			0.021
	Swedish charcoal iron	Cleaned	0.03	0.03	0.019	0.022	0.02			0.063

* Committee of the Institution of Civil Engineers.(1)

109. Immersion Tests by the Committee of the Institution of Civil Engineers (British).—These tests were started in 1916, and reports were published at intervals under the title of "Deterioration of Structures in Sea Water."(130,155,205,235,260,263,353,396) The program included alternate-wet-and-dry and complete-immersion tests. Specimens of various steels and irons in the form of rolled bars (24 × 3 × 0.5 in.) were exposed at Auckland, New Zealand; Colombo, Ceylon; Halifax, Nova Scotia; and Plymouth, England. Three hundred and seventeen bars were tested at Auckland and 204 at each of the other three localities. The condition and the chemical composition of some of the bars are given in Table 60.

The conclusions regarding the effect of copper are summarized by the committee as follows:[205,235]

After 5 years' exposure the two cupriferous steels *G* and *H* (Table 60), containing 0.63 and 2.18 per cent copper respectively, lost less in weight than the low-copper steel *F* with 0.09 per cent copper. The 2 per cent copper bar was more deeply pitted. When both the loss in weight and the pitting are considered the copper bars have a slight advantage. The metal with the lower copper content (0.63) lost less in weight than the metal with the higher copper content (2.18).

Inspection after 10 years' exposure indicated that the copper steels were still superior to mild steel and wrought iron.[353] A summary of the results of the entire tests has been planned.[384]

110. Other Total-immersion Tests.—Tests were made by Bauer[109] in Germany on small specimens of the materials described on page 224. The results indicated that copper has no effect on the corrosion rate of iron and steel immersed in distilled water, tap water, and subjected to intermittent immersion in sea water. Later tests by Bauer, Vogel, and Holthaus[254] could be interpreted to show that the presence of copper in varying amounts up to 1.0 per cent slightly reduced the corrosion of steel immersed in various waters.

British tests of relative corrodibilities of various commercial forms of iron and steel included a steel that contained 0.15 per cent copper. No marked difference due to copper was observed in tap- and sea-water tests.[127,135,179,233]

111. Effect of Copper on Corrosion of Pipes.—As reported by Hamilton,[75] the Providence (R. I.) Gas Company made some tests of sheet and pipe specimens of wrought iron and steel containing various amounts of copper. The specimens were immersed in a hot-salt-water condenser operating at 70°C. (160°F.), and in a fresh-water condenser at 60°C. (140°F.). Copper was thought to be beneficial.

A number of tests on pipes are described by Speller, who wrote in his book[172]:

The author has cooperated in the making of many service tests on copper- and non-copper-bearing pipe in hot and cold domestic water lines. Lengths of copper-bearing steel pipe were alternated with ordinary steel pipe in each case so that all variations in service conditions affected the two classes of metal equally. On the whole, these tests have shown no advantage in favor of either class of material.

TABLE 61.—INFLUENCE OF COPPER ON THE CORRODIBILITY OF STEEL WATER PIPE*

When removed	Location and kind of service	Duration of test	Authority and references	Maximum penetration, inches per year†	
				Regular	Copper bearing
1910	New York City bath; hot water	2 yr.	College of the City of New York	0.054	0.047 (Cu 1.0)
1914	National Tube Co. laboratory, McKeesport, Pa.; hot-water service	2 yr.	National Tube Company	0.019	0.018 (Cu 0.15) 0.020 (Cu 0.35) 0.021 (Cu 1.00)
1917	New York City baths; return steam lines	2.5 yr.	MacGregor, Columbia University‡	0.011	0.011
1918	Brown University; hot-water lines; average temperature 70°C. (160°F.), 2-in. pipe 6.5 ft. long	11 mo.	Kenerson, Brown University§	0.081	0.091
1919	Harvard University; hot-water lines, average temperature about 70°C. (160°F.)	3 yr.	Whipple, Harvard University‖	0.015	0.022

* Speller.(172)

† The average value for the different pieces in each test.

‡ MacGregor.(169)

§ Kenerson.(167)

‖ Reference.(107)

Typical results of a few of these investigations are given in Table 61.

According to Speller, in the corrosive underground saline waters of southern Texas copper-bearing steel has shown some advantage over ordinary wrought iron or steel. Experiments made by the National Tube Company, in which steel tubes of several copper contents were coupled together in the same wells, indicated that the resistance to corrosion increases materially with the copper content up to about 1 per cent, as indicated in Fig. 118.

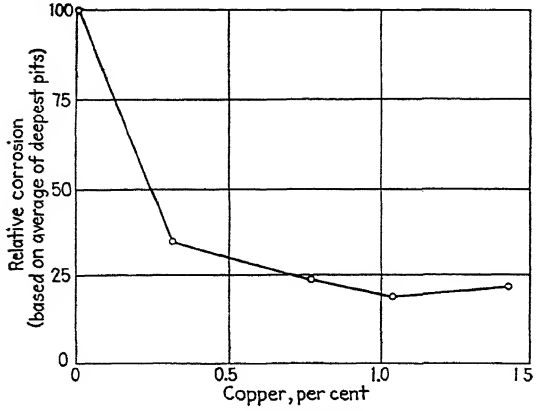


FIG. 118.—Service tests on oil-well seamless steel tubing in southern Texas. Two-inch 0.15 per cent carbon steel tubing of variable copper content. Tested for 343 days. (*Speller.*[172])

In a recent symposium[341] on cast iron it was stated that: "In practical applications cast iron containing from 0.5 to 1.0 per cent copper has been used successfully in many cases, such as pipe lines in oil-refinery work. Copper-bearing cast iron is superior to plain cast iron in atmospheric corrosion."

Since copper steel is cathodic to ordinary steel, to prevent electrolytic action it may be advisable to avoid contact between ordinary and copper steel, especially in saline waters.[172]

According to the Reports of the Corrosion Committee of the American Petroleum Institute,[181,189,217,218] copper-bearing steel tubing and casing have been successfully employed, with copper as high as 1 per cent, in parts of the Gulf Coast Field. Steel containing 0.5 per cent copper or more was used extensively in the construction of oil-storage tanks.[218]

Tests were recently made at various American refrigeration plants on lengths of 1-in. diameter pipes exposed to the action of calcium and sodium brines under various conditions.[192] It was found that the corrosion rate of steels containing 0.25 per cent copper was 75 per cent that of ordinary iron and steel pipes.

112. Copper Steel in Ship Plate.—The question regarding the use of copper steel for ship plate has aroused considerable interest. Claims have been made that copper imparts to steels an outstanding resistance to corrosion in sea water. For example, the surprisingly good state of preservation of a bottom plate of the *Leviathan*, which had stood for 3 years in New York harbor, was attributed to the presence of about 0.15 per cent copper.[147,152] Later investigations, however, indicate that the differences in the service conditions, such as mechanical action of water currents and degree of aeration, account satisfactorily for alleged differences in the corrodibility of steels.[244,248,327]

Corrodibility of steel in sea water is also affected by the variations in the internal and external conditions of the metal itself and the contact with other metals. These factors are particularly important in the corrosion of riveted ship plates because of the strains induced by cold working or loading, heating gradients, and differences in contact. According to Bennett,[160] tests made for the Society of Naval Architects and Marine Engineers indicated that, as the copper content in rivet steel increases from 0.01 to 0.32 per cent, the position of the metal in the electromotive series is lowered; consequently, the higher the copper content of the rivet metal, the more electronegative, *i.e.*, corrosion resistant, is the rivet in contact with steel of ordinary shipbuilding quality when immersed in sea water. It was recommended that the copper content of steel rivets be specified from 0.20 to 0.30 per cent with a maximum carbon content of 0.20 per cent, and that, on the other hand, the plates should have their copper content not over 0.15 per cent in order to render the plate slightly electropositive to the rivet.

113. Other Tests.—According to a pamphlet issued by the National Canners' Association,[134] "the results obtained with the use of copper do not offer any justification for addition of copper to steel for the manufacture of tin plate, neither do they constitute a reason for specifying the absence of copper in such steels." Copper does not seem to have any influence on the resistance of tin plate toward acids of canned products.

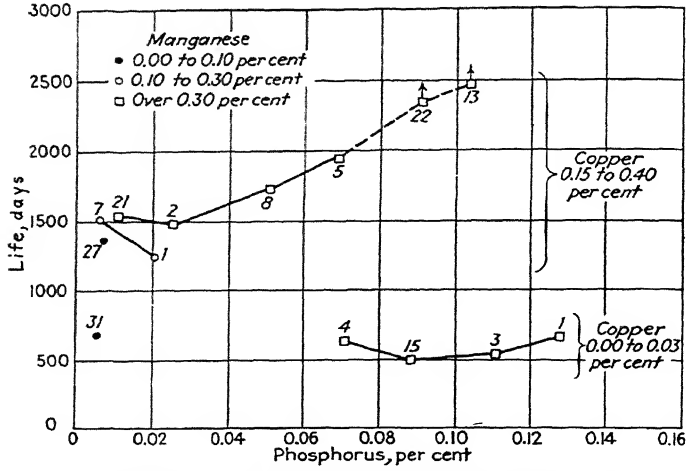


FIG. 119.—Pittsburgh tests, 22-gage sheets, showing effect of phosphorus, copper, and manganese. (*Kendall and Taylerson.*[236])

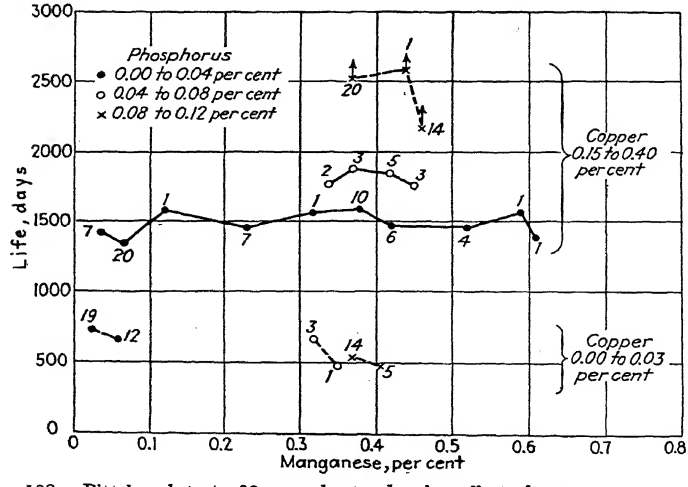


FIG. 120.—Pittsburgh tests, 22-gage sheets, showing effect of manganese, copper, and phosphorus. (*Kendall and Taylerson.*[236])

114. Effect of Manganese, Phosphorus, and Sulphur on the Corrosion of Iron and Steel.—The influence of copper might be considerably affected by other common elements usually found in commercial materials. According to Buck,[78,80,90,111] sulphur increases the atmospheric-corrosion rate of iron and steel, and the harmful effect of sulphur in amounts as high as 0.055 and 0.14 per cent is alleged to be neutralized by the addition of 0.12 and 0.25 per cent of copper respectively. Knight[357] also stated

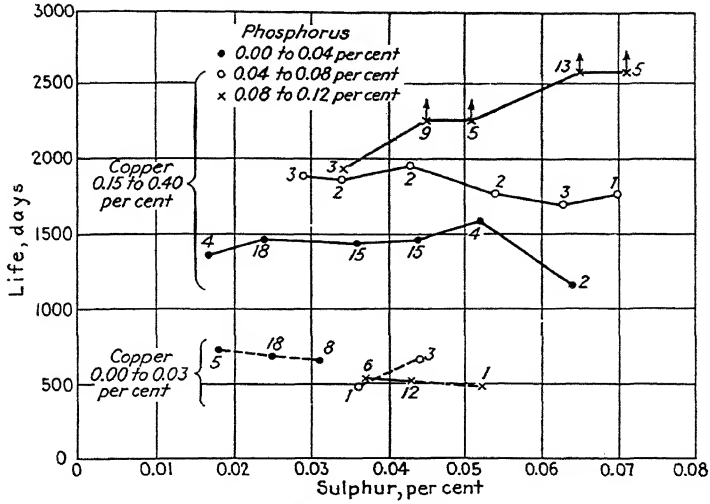


FIG. 121.—Pittsburgh tests, 22-gage sheets, showing effect of sulphur, copper, and phosphorus. (*Kendall and Taylerson.*[236])

that copper counteracted the harmful influence of sulphur on the corrosion resistance.

From the statistical analysis of the data obtained in the A.S.T.M. tests Kendall and Taylerson[236] drew the following conclusions regarding the effect of manganese, phosphorus, and sulphur on the atmospheric corrosion of copper-bearing steels:

Phosphorus combined with copper has a very beneficial effect.

Manganese and sulphur, within the limits of compositions involved, seem to have little, if any, effect either way.

High copper combined with high phosphorus apparently counteracts any bad effect due to sulphur.

The evidence for these statements is shown in Figs. 119, 120, and 121, which were plotted by Kendall and Taylerson from the data reported by the A.S.T.M.

The effect of the variations in manganese, sulphur, and phosphorus content on underwater corrosion is not so apparent as in the case of the atmospheric tests; the curves were so erratic that no conclusions could safely be drawn regarding the effect of any particular element.

In British patent 365,538 of January 18, 1932, it is claimed that high-phosphorus steels containing copper or copper and silicon have a high resistance to atmospheric corrosion. While the question of the influence of the phosphorus content on the corrosion resistance of copper steels has not been widely discussed, the suggestions of Kendall and Taylerson are probably being studied, and further corroboratory or contradictory evidence is likely to be available later.

The British investigation of the deterioration of structures by corrosion revealed some indications of the injurious influence of sulphur on the corrodibility of steel in sea water as well as in atmosphere.[205]

C. UNDERGROUND CORROSION

The process of corrosion of iron and steel buried in soils embraces the characteristics of both atmospheric and submersion types of corrosion but is enormously complicated by the presence of many variables, such as character of soils, chemical composition, quantity and rate of flow of underground water, access of air, and stray electric currents. The study of the effect of each of these variables and the interpretation of their influences in each particular test are extremely difficult. Experience has indicated that the effect of these external factors far exceeds the influence of small variations in the content of common elements, including copper, usually present or alloyed with iron or steel.

115. Early Investigations.—Campbell,[74] in 1914, found that 0.45 to 0.60 per cent of copper considerably increased the corrosion resistance of Bessemer and open-hearth mild steel buried in soil or in cinders. In another series of experiments specimens of charcoal iron, ingot iron, open-hearth steel, and copper-bearing open-hearth steel with 0.43 and 0.98 per cent copper were set in clear sand, clay, alkali soil, bituminous-coal cinders, etc. Observations made every 3 months failed to show any definite superiority of any of the materials used in the tests.

In the same year Hamilton[75] reported that a pipe of copper steel containing 0.21 per cent copper, laid in gravel soil in 1867 and removed in 1911, was found in a remarkably good state of preservation. Further experiments indicated that sheet and pipe made of copper steels containing 0.64 and 0.77 per cent copper were more resistant to underground corrosion than a steel with lower copper content (0.16 per cent).

The tests of railroad steel ties[306] referred to on page 239 showed that the loss in weight of the parts of the ties buried 9 years in ash ballast was 9.1 and 20.9 lb. for 0.25 per cent copper steel and a copper-free steel respectively, the total weight of new ties having been 204 lb.

116. German Underground-corrosion Tests.—These tests, started in 1914, were made by Bauer on the same materials as

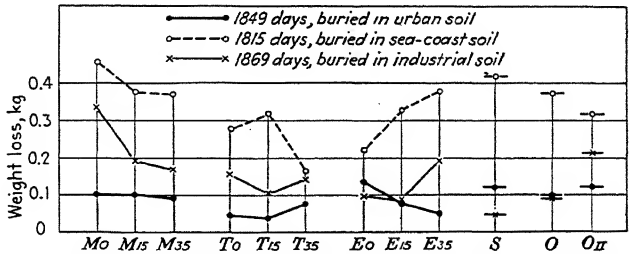


FIG. 122.—Results of German underground (buried) corrosion tests. (*Bauer.*[109])

described on page 224. The sheets were buried for 5 years in three different locations: (1) in sand near Berlin, (2) in sea sand, (3) in sand in an industrial locality. According to the report by Bauer,[109] the results, represented graphically in Fig. 122,* "do not warrant any definite conclusions regarding the effect of copper. The corrosion was most severe in the sea sand. The only material that showed the beneficial effect of copper in all three conditions of exposure was the steel of series 'M.'"

It may be noted, however, that in the majority of cases the corrosion loss is reduced somewhat by the addition of 0.15 per cent copper; further increase in copper content produces somewhat erratic results, appearing sometimes beneficial, sometimes injurious. The variations in phosphorus, and particularly sulphur content, may account for some of the irregularities.

* Subscripts 0, 15, and 35 represent approximate copper content in hundredths of 1 per cent.

Bauer's data, grouped according to the kind of steel regardless of the character of soil, indicated that the increase in copper content up to about 0.25 per cent considerably reduced the corrosion rate of steels, further additions of copper having little effect. Figure 123, compiled by Daeves,[163] also indicates that basic Bessemer steel was considerably more resistant to corrosion than the open-hearth steel, although the relative improvement due to copper was nearly the same for both kinds of steel.

117. Soil-corrosion Investigation by the U. S. Bureau of Standards.—The investigation has been under way since 1922 and included tests of a large variety of ferrous and non-ferrous materials. Among the ferrous pipe materials were copper-

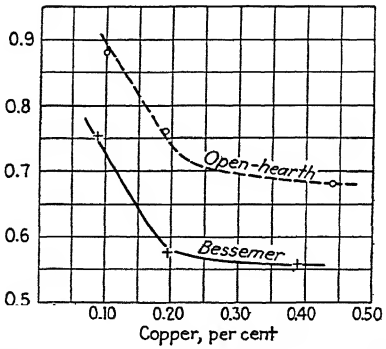


FIG. 123.—Influence of copper on the corrosion resistance of steel buried in soil. German tests.

bearing steels. The specimens were buried in trenches in some 50 different locations representing various types of soils and various climatic conditions.

The reports on periodical inspections[168,186,239,294,295,397] indicated that none of the pipe materials used in the tests was superior to others under all soil conditions. Observations after 2 years' exposure revealed a very erratic behavior of copper steels. Later inspections showed that corrosion and pitting varied so much with the locality that no generalizations were possible. It was evident that soil characteristics and variability of external factors, rather than differences in chemical composition, and specifically the presence or absence of copper, determined the type and extent of corrosion. The rate of corrosion was found to change very irregularly from year to year. In moist soils a decrease in the corrosion rate with time was noted.

As an illustration of the general statement that no appreciable difference is observed in the corrosion of low-copper and non-copper steels buried in soils the following figures are given:[239]

Steel	Composition, per cent					Average loss in 47 soils, oz. per sq. ft. per year		
	Mn	P		Cu		First 2 years	Next years	Next years
Open-hearth, copper-free	0.12	0.41	0.043	0.036	0.0	0.87	0.69	0.63
Open-hearth, copper steel	0.07	0.24	0.008	0.032	0.22	0.89	0.69	0.64

From the results of the Bureau of Standards' tests Logan,[362] in 1933, concluded:

The data on underground corrosion indicate quite definitely, however, that all of the commonly used ferrous pipe materials corrode at nearly the same rate under the same soil conditions.

Copper-bearing steel, however, does not appear to be superior when buried in soil, perhaps on account of the limited supply of oxygen.

D. PROTECTIVE COATINGS

Iron and steel fabricated into sheet, plate, structural shapes, or other products not subjected to wear or abrasion are rarely used without artificial protective coatings when subjected to the corrosive action of the atmosphere or other agents. All of the common coatings—painting, galvanizing, and electroplating—are designed to protect the surface of the underlying metal. As soon as the coating has failed, the metal is exposed to atmospheric attack, and the damaged or failed coating may have no influence, may accelerate, or retard somewhat the rate of corrosion of the underlying metal, depending on the nature and the direction of the electrolytic action between the coating and the metal.

If the coating is renewed regularly and its continuity is maintained, the corrodibility of the base metal is of no importance. However, as soon as the coating has been entirely destroyed, or has suffered a local damage, and is not renewed, further service of the metal will depend on its own ability to resist the corrosive attack. The life of a coated iron or steel article will, under such

conditions, be determined by the sum of the two factors—protection by the coating and the corrosion resistance of the metal. The corrodibility of the material decides how frequently repainting or recoating is necessary. Frequently it is rust which pushes away the paint and thus causes premature failure.

One of the most important factors determining the life of coatings is their ability to adhere to the metal. It is from this point of view that the influence of copper on the effectiveness of protective coatings should receive consideration.

118. Painting.—It has been claimed that paint adheres better to copper steel than to copper-free steel.[123,219,252] Describing the tests conducted by the Bessemer and Lake Erie Railroad on copper and non-copper steel plates in car bodies, Unger[220] reported:

> The most noticeable difference in the two kinds of steel at the end of two years of service was the condition of the paint. The paint was adhering much better to the copper steel than to the plain steel. In many cases the copper steel would be well protected by the paint, while practically no paint remained on plain steel in similar locations. This resulted in a plain steel being corroded to a greater extent on the outside of the car body than the copper steel, as indicated by considerably more and deeper pitting on plain steel. The influence of the two kinds of steel has also been a factor in the cost of maintenance.

In a recent paper dealing with exposure tests of painted sheets of ferrous materials Britton and Evans[345] concluded:

> The results, so far as they go, serve to bear out the superiority of copper steel over ordinary steel, which has been indicated by more elaborate tests in Germany and America. They also point to the good behavior of wrought iron. This is apparently due to the infrequency of specially susceptible points, the greater tendency to passivity, and the convenient character of the scale. Actually there are two scales on wrought iron; one comes off very easily, while the other is so adherent that paint can be applied over it without causing any of the undesirable effects often met with when paint is applied to steel without previous descaling.

Daeves[283] also cited results to prove that painted copper steels have a corrosion resistance superior to painted copper-free steels. He concluded, however, that the nature of the surface painted may have more influence on the corrodibility than the composition of the base; mill scale in particular tends to cause rapid loss by corrosion because it causes the paint to blister.

According to some recent results reported by Daeves[283] in reply to discussion of his paper, in contaminated water copper increases the life of painted steel, even though it has practically no influence on the life of uncoated steel submerged in water.

119. Galvanizing.—There are more reasons (than in the case of painting) to expect that some relation may exist between the effectiveness of the protection by zinc coating and the presence or absence of copper, because this is a case of contact between two metals. The solubility, diffusion, and electrolytic relation between the zinc and the iron may be slightly changed by the presence of copper in the steel, and this may have some influence on the adherence and, perhaps, on the constitution of the zinc layer, which may be reflected in the durability of the coating. On the other hand, after the iron has been exposed to the action of a corrosive medium because of a partial failure of the coating, the alleged change of the electrolytic potential of the iron toward the negative side when copper is added may, obviously, influence the course of electrolytic action between the iron and the zinc.

From tests made on wires of copper and non-copper steels (containing 0.15 to 0.23 and 0.03 per cent copper respectively) exposed to the influence of industrial atmosphere for 18 to 21 months, Daeves[197] concluded that copper produces a marked improvement in the corrosion resistance of black and galvanized wires. The wires were allowed to corrode further, after the zinc coating had been entirely destroyed by corrosion. It was observed that the first coloration and darkening of the zinc coating appeared sooner on the copper-free than on the copper-bearing wires. Another observation of greater importance was made, *viz.*, that the destruction of the zinc layer is considerably retarded by the presence of copper in the steel. Daeves claimed that the beneficial action of copper in increasing the life of galvanized wire is not confined to its effect in increasing the corrosion resistance of steel but is also manifested in improving the protective properties of the zinc coating. Other results reported by Daeves[283] also show that copper is beneficial in increasing the corrosion resistance of galvanized wire.

Observations of Groesbeck and Tucker[201] are not in agreement with the conclusions drawn by Daeves. From the results of some accelerated corrosion tests they concluded that the presence of 0.20 per cent of copper in steel produced no appreciable effect on the life of the zinc coating as compared with that

of the coating on non-copper-bearing steel. The quality of the coatings was evaluated on the basis of "accelerated atmospheric" corrosion tests (5 hr. exposure to corroding atmosphere, 1 hr. exposure to water spray, and 18 hr. drying) and by spray tests in sodium chloride and ammonium chloride solutions. The corroding atmosphere consisted of 94 parts of air, 5 parts of CO_2, 1 part of SO_2, saturated with water vapor.

120. A. S. T. M. Tests of Metallic Coatings.—The widespread interest in the corrosion resistance of various metallic coatings has manifested itself in the inauguration of an extensive series of field tests by the American Society for Testing Materials in cooperation with several interested organizations. The tests were started in 1926 as a sequel to the tests on uncoated materials and, in addition to sheets, included structural shapes, wire, and various kinds of hardware. The specimens with coatings of varying thickness and without coating were exposed to five different types of atmosphere.[162,176,196,231,259,282,316,346]

The outcome of these tests will be of great interest with reference to copper steels, since both copper-bearing and non-copper-bearing irons and steels were included in the tests. The results of observations reported up to date (1933) relate mainly to the behavior of coatings. Only a few failures of the base metal have been reported, and the data available are insufficient to detect any differences in the life of sheets due to variations in copper content.

The large number of specimens tested will furnish sufficient data to make possible a statistical estimation of the effect of variables including the influence of copper. It is anticipated that when the final reports of the investigation become available the question whether copper in iron or steel has any effect on the properties and life of zinc coating will be definitely answered.

E. THEORIES

Any acceptable theory for the explanation of the effect of copper should be consistent with the observed facts—that a marked improvement in resistance to atmospheric corrosion occurs by raising the copper content from zero to about 0.20 per cent with but slight, if any, gain above that content, and that (beyond an apparently improved behavior of 1 per cent copper steels in oil-well brines) the copper steels, by and large, behave no better and no worse in submerged corrosion, in fresh or sea

water, than do steels free from copper, and when buried in soils the copper steels again act just like other steels.

Obviously, one difference in these conditions is that in atmospheric exposure the corrosion products dry out completely at frequent intervals, while in immersed or buried conditions they have no opportunity to dry.

121. Theories Regarding the Mechanism of Corrosion of Copper Steel and Iron.—Guertler[202] in the first Campbell Memorial Lecture emphasized the importance of the formation of solid solutions if the metal itself is to be corrosion resistant. He asserted that ferrous alloys can be made resistant to acids by the addition of nickel, chromium, and copper because these metals are nobler than the iron, and when in solid solution with it they increase its "nobility." However, when copper is added in amounts exceeding the solubility limit, the excess copper particles might act as cathodes of the local galvanic elements to accelerate the corrosion or solution of the iron. Guertler stated that in the case of iron-copper alloys the principal cause of the favorable action of copper when all the copper is in the solid solution is the formation of a protective layer of oxide which is more tenacious and better adhering than the rust layer of copper-free steel. When the excess copper forms a second phase the alloy is not homogeneous; the rust layer will be discontinuous and not effective in preventing the electrolytic solution of iron.

The increase in nobility of iron with addition of copper was claimed by Bauer,[109] Watts,[124] Buck,[111] Schenck and coworkers,[247] and others. From a study of etching figures of alloys Svetchnikoff[271] advanced the idea that the solution rate of metallic solid solutions can be related to the degree of distortion of the space lattice of the alloy by the added element. Copper was found to produce less space-lattice distortion than silicon, per cent for per cent, and, therefore, was assumed to impart better corrosion or solution resistance to iron.

The effect of copper in improving the protective properties of the rust layer of iron and steel was noted by Bauer,[109] Richardson,[119] Buck,[111] Evans,[165] Creutzfeldt,[177] and others. Buck[111] claimed that copper steel is less electropositive to the first film of rust than copper-free steel and is, therefore, more resistant.

Borgmann[314] suggested that the rise of the "critical corrosion humidity" (humidity above which rapid attack of the iron takes

place; approximately 40 per cent relative humidity at normal temperatures) due to copper is partly responsible for the increase in atmospheric-corrosion resistance of steel.

Bell and Patrick,[110] in 1921, proposed a tentative explanation of the retarding effect of copper on solution rate of iron in hydrochloric acid, according to which the copper dissolved from the steel is precipitated in a finely divided state on the surface of the steel. Since it is more soluble than the copper contained in the solid solution in the steel, it is redissolved, then redeposited, etc. This intermittent solution and precipitation of copper supposedly retard the solution of the iron.

Borgmann and Evans[387] recently suggested that, in the corrosion of copper steel, copper when dissolved is redeposited as metal at the originally anodic points and will favor a change in polarity; this will cause the attack to extend laterally until the whole surface is covered with corrosion product, after which attack is likely to slow down.

All these theories have been criticized, the evidence for most of the conclusions having been insufficient or contradictory, and no satisfactory explanation had been evolved until the work of Carius and Schulz[229] and of Carius[258,280] was published.

122. Mechanism of Corrosion of Copper Steels. *Investigation of Carius.*—A very thorough investigation of the mechanism of corrosion of copper steels in atmosphere, water, and various salt solutions was made at the laboratories of Vereinigte Stahlwerke in Germany.[229,258,280] The process of corrosion of copper steel is described as follows: Copper atoms uncovered by the dissolution of the surface layers of iron are first oxidized to copper ions. The copper ions are in turn reduced and deposited on the surface as metallic copper. It was found that the deposition of copper is independent of the acidity of the solution within the range of pH from 4 to 9, but the form of the deposited copper varies, depending on the chemical composition, concentration, and acidity of the corrosion medium. In the atmosphere when the steel is wet by rain or dew plus dissolved atmospheric gases the copper deposits in the form of a uniform continuous film, while in aqueous salt solutions it precipitates in the form of finely divided particles forming a porous discontinuous layer of sponge copper. This difference in the form of the copper deposition has a bearing on the further course of the rusting process and results in an entirely different effect on the corrosion resistance of copper

steel. Two processes of rusting should, therefore, be distinguished: (1) rusting in distilled water and in the atmosphere, and (2) rusting in various salt solutions.

123. Rusting of Copper Steels in Distilled Water.—Copper steel, when immersed in distilled water, becomes covered with an iridescent film. The initial iron oxide and hydroxide colors of light yellow to green change to orange, to blue, and to black, and in places metallic copper is deposited. With time the colors disappear, and a black layer of cupric oxide takes their place. This oxide layer is at first smooth and adherent, but with time it begins gradually to deteriorate and changes into a loose powdery and porous copper oxide layer, which allows the free access of water to the surface of the steel. The water again attacks the steel surface and forms a new copper film, and the process is thus repeated (see Fig. 124).

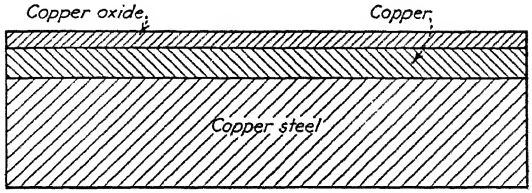


FIG. 124.—Formation of copper and copper oxide layers on the surface of copper steels in atmosphere or distilled water. (*Carius.*[258])

Because of the heterogeneity of the steel surface the attack does not start simultaneously over the entire surface, and the copper film is not uniform; small areas of the steel are in the various stages of the rusting process, and the rusting and deposition of the copper film move from place to place over the entire surface of the steel. The formation of the copper film is disturbed by the local currents which set up on the boundaries between segregated and non-segregated metal. The areas of purer metal, in the beginning of the rusting process, are covered with a copper film, and a stronger rust formation occurs at the boundaries between the copper film and the iron of the segregated areas. If the rust is removed, the steel surface appears etched out in grooves along the boundaries between the segregation and the copper zones, while the covered zones of the metal stand out in relief. In reviewing this paragraph Schulz said that these phenomena can

occur on homogeneous faces and that segregation alone cannot account for the non-uniform attack.

124. Rusting of Copper Steels in Atmosphere.—The rusting process in the atmosphere is similar to that in distilled water, but the copper oxide layer is more adherent and continuous (in the atmospheric-corrosion process). The impervious copper oxide layer shuts off the access of moisture of the air to the steel surface and leads, therefore, to the protection of the steel.

The formation of copper film and the presence of copper in the oxide film were actually proved by chemical analysis.[229,312]

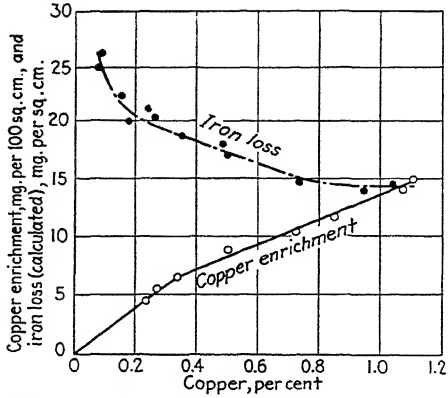


FIG. 125.—Relation of copper enrichment in the black oxide layer to copper content of steel and calculated iron loss after 9 months' exposure to atmosphere. (*Carius and Schulz.*[229])

Carius and Schulz[229] showed that the copper content of the oxide layer of copper steel increases with the copper content of the steel, while the loss of iron from the underlying metal decreases (Fig. 125).

125. Rusting in Aqueous Salt Solutions.—Observations showed that in salt solutions, tap water, sea water, etc., the steel becomes covered with a porous permeable layer of spongy copper. Small particles of copper form an electrolytic cell with the steel, whose action manifests itself in the increased solubility of the steel. The current strength of these cells cannot be determined on account of the difficulty in measuring the surface of the copper crystals. However, by using artificial iron-copper cells it was estimated to be about 1.5×10^{-5} amp. per sq. cm., which corresponds to an iron loss of about 0.4 mg. per sq. cm. per day.

It has been found that the strength of these minute cells depends on the oxygen content of the solution, which depolarizes the hydrogen liberated at the copper crystals. The polarization process impoverishes the oxygen concentration near the specimen. At the same time more ferrous ions are carried into solution, and ferrous hydroxide is formed. Since the oxygen content near the specimen is not sufficient for complete oxidation of the ferrous hydroxide, the oxidation process remains at an intermediate stage, which is indicated by the appearance of a green "sorption compound" consisting of ferrous and ferric hydroxides. This gelatinous hydroxide covers the steel as a tenacious layer and,

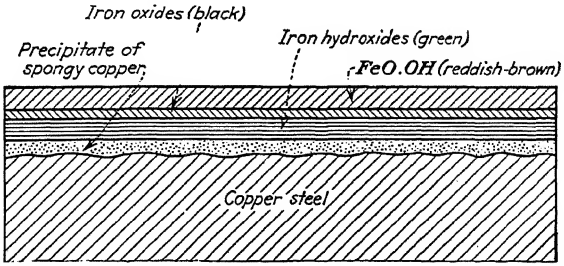


FIG. 126.—Formation of layers on the surface of copper steel immersed in an aqueous salt solution. (*Carius.*[253])

gradually hardening, shuts off the access of water and oxygen to the surface of the steel. The decrease in the oxygen polarization current due to this shutting off results in decreased dissolution of iron and in decrease in the oxygen consumption. The oxygen diffusing from the surface of the solution is now used up in the oxidation of the green hydroxide to black ferro-ferric oxide, and further to brown ferric hydroxide. Both these intermediate products of oxidation are porous and granular; the iron is again exposed to water and oxygen. The galvanic action of the iron-copper cells begins again with the renewed dissolution of iron, until the corrosion is again interrupted by the formation of the green layer.

The action of this protective green gelatinous sorption compound commences to check the corrosion after two or three months' exposure. This may be seen from the difference in the nature of the surface of copper and non-copper steels. The surface of copper steel is smooth, uniformly eroded, while that of copper-free steel is rough, fissured, and strongly eroded. The

layers which are formed on copper steel immersed in artificial sea water are shown schematically in Fig. 126.

Complete cessation of the corrosion of copper steels does not occur because of the porosity and constant change of the green hydroxide layer.

In Fig. 127 the resistance of electrolytic iron to corrosion in artificial sea water is compared with that of a 1 per cent copper basic Bessemer steel. During the first three to four months electrolytic iron was more resistant; however, between the fourth and fifth month the protective action of the green hydroxide

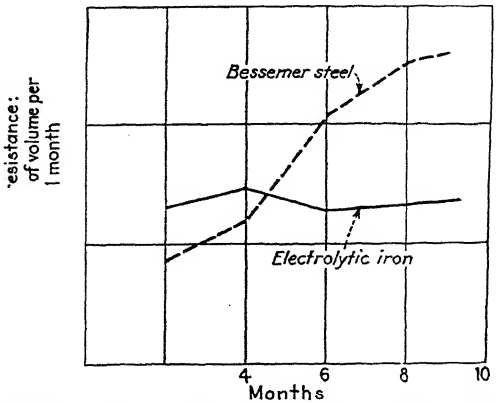


FIG. 127.—Corrosion resistance of electrolytic iron and copper steel in artificial sea water. (*Carius and Sch*

became so active that the copper steel became more resistant than the iron under the particular conditions of the test.

In summarizing the work of Carius, it may be said that the protective action of copper is due not to the increased resistance of steel itself when copper is added, but to the protective action of the copper and copper oxide layers deposited on the surface of steel.

126. Means of Increasing the Protective Action of Rust Layers. Further investigation[280] showed that in sea water the green hydroxide layer is disturbed by the action of sodium and calcium chloride. The rust layers in magnesium-bearing water tend to flake off and expose the new fresh surfaces of steel to the action of water. These considerations led to further investigation with the object of producing a steel which would form a stable waterproof protective layer in sea water. It was alleged that this

could be accomplished by adding 0.1 to 0.2 per cent aluminum to steel, particularly to a 0.25 per cent copper steel. Comparative corrosion tests were made on 0.10 to 1.0 per cent aluminum, 0.15 to 1.0 per cent copper steels, and copper-free steels. The results of 14 months' tests in artificial sea and tap water indicated copper-aluminum steels to be superior to copper and copper-free steels. A content of 0.11 per cent aluminum and 0.20 per cent copper was found to be sufficient to produce good protective action. The action was found to begin between the seventh and eighth month after exposure; between the eighth and fourteenth month practically no loss in weight was observed. Information is lacking as to how this laboratory observation agrees with actual sea-water service.

It was found that in the atmosphere copper-aluminum steels become covered with a brown crust which hardens on drying and becomes whitish brown. Underlain by copper, it adheres firmly to the steel. This coating, however, was not permanent, and after one year's exposure the corrosion proceeded as in plain copper steels.

127. Effect of Copper on Solubility of Iron and Steel in Various Media.—An enormous amount of work was done with the object of determining the effect of copper on the solubility of iron and steel in various electrolytes, tap, river, and sea water, molten salts, salt sprays, etc. Because of the great number of variables mentioned above the results are very discordant, as one would expect, and forming any conclusions is extremely difficult. Many of these tests, particularly the earlier ones, were made because it was believed that "accelerated" acid tests provide reliable information regarding the behavior of iron and steel in actual service. Since, however, this opinion has been proved to be erroneous, these tests have become valueless and will not be presented here in detail.

According to the American Society for Testing Materials in 1928:

> Notwithstanding the fact that this Committee, in its annual report of 1909, pointed out as clearly as it could that the tentative suggestions made by it in 1907 as to the conditions for carrying out the so-called acid corrosion test were not to be considered a recommendation of the test, and that the results of such test are unreliable as truly measuring the tendency to natural corrosion, the name of the American Society for Testing Materials continues to be used as having recommended the

acid corrosion test, and by inference as having endorsed the same. For this reason the Committee desires at this time to again disclaim any recommendation or endorsement of the acid test as a measure of natural corrosion, and to point out that any use of the name or authority of the American Society for Testing Materials in this connection is unwarranted.

Among the numerous investigations on the effect of copper on the solution rate of iron and steel the following are most important: Walker,[64] Burgess and Aston,[66] Buck,[69] Aitchison,[77] Kalmus and Blake,[83] Richardson,[104,105,106,119] Watts and Knapp,[125] Bell and Patrick,[110] Cushmann and Coggeshall,[114] Aupperle and Strickland,[108] Bauer,[109] Friend,[127] Hadfield,[129] Utida and Saitô,[159] Evans,[165] Grison and LePage,[182] Denecke,[198] Endo,[199] Schulz,[216,248] Rawdon,[244] Mattheis,[266] Bauer, Vogel, and Holthaus,[254] Daeves, Schulz, and Stenkhoff,[284] Marzahn and Pusch,[298] Bardenheuer and Thanheiser,[312] and the American Society for Testing Materials.[282]

From the mass of information available on the "accelerated-corrosion" or acid-solution tests the following generalizations regarding the effect of copper on the solution rate of iron and steel may be made:

Small amounts of copper improve the resistance of iron and steel to attack by sulphuric and hydrochloric acids.

In nitric acid tests the rate of solution is increased by copper.

Tests in various salt solutions indicate that copper has no appreciable effect on the rate of solution of iron and steel.

It has been noted that the resistance of iron and steel to attack by acid, salt, and alkaline solutions is increased as the copper is increased to a certain content and decreases somewhat as the copper content exceeds this concentration. This critical copper concentration was stated by various investigators as being between 0.35 and 1 per cent.[136,159,199,298]

F. AUTHORS' SUMMARY

1. Long-time field and service tests have proved definitely that the life of iron and steel exposed to the corrosive action of the atmosphere is materially increased by the addition of 0.15 to 0.25 per cent copper. Further increase in copper content does not seem to be of any appreciable benefit or harm.

2. Field tests indicated that the effect of copper on the corrosion of iron and steel totally or partly immersed in various kinds of water is much less pronounced than in the case of atmospheric

exposure and may be completely masked by variations in external conditions. Although it is evident that the effect of copper is small, the results obtained by various groups of investigators are somewhat contradictory. While the A.S.T.M. tests indicated no appreciable effect of copper, the German and the British tests appear to have indicated a very slight advantage in favor of copper-bearing steels.

3. The influence of copper on the corrosion of iron and steel buried underground has not been investigated so fully as that on atmospheric or underwater corrosion. From the data available it is evident that the effect of copper is not very pronounced and is secondary to the influence of variations in numerous external factors. It may be safe to say, however, that on the whole the effect of copper, if any, is not detrimental.

4. It has been claimed that the advantages of adding copper are augmented when iron or steel to be used for service under exposure to atmospheric corrosion is painted or galvanized. It was claimed that paint adheres better to copper steel and that zinc coating on copper steel lasts longer than on non-copper steel. These statements, however, are open to argument and should not be accepted unconditionally until further experimental evidence is available.

5. A great deal of experimental work has been done with the object of determining the effect of copper on the solubility of copper steel in various electrolytes. The rate of solution in various electrolytes does not appear to be influenced by copper to any appreciable extent. It has been found that small amounts of copper improve the resistance of iron and steel to the attack by sulphuric and hydrochloric acids and decrease their resistance to nitric acid. However, such material is attacked far too rapidly to be of use for acid containers, and the observation is of academic, not practical, interest.

6. The behavior of copper-bearing and non-copper-bearing iron and steel in acid or salt solutions bears no relation to their relative behavior in atmospheric or underwater corrosion, and these so-called "accelerated tests" are worthless for prediction of life under other conditions.

7. The protective action of copper is due to the formation of copper and copper oxide films on the surface of iron or steel. This action varies with the variations in external conditions and may become injurious when the copper is deposited in discontinuous patches or separate particles.

CHAPTER X

COPPER IN CAST IRON

Manufacture and Structure of Copper Cast Iron—Influence of Copper on Properties of Cast Iron—Copper in Malleable Cast Iron—Copper in Complex Alloy Cast Iron—Authors' Summary

Previous to 1900 there were few published investigations on copper in cast iron. The earliest recorded work seems to be that of Mushet,[4] reported in 1835; this was followed by the work of Krilowski,[6] in 1839. Copper in cast iron was mentioned by Percy,[11] in 1864, but it was not until 1895 that the first detailed investigation was made by the Russian metallurgist Lipin.[33] His work, although of interest, led neither to further study nor to the commercial use of copper cast iron. In the past 12 years, however, considerable information has accumulated. Nearly all of this deals with the effect of copper on the properties of gray and malleable iron; very little is known about white cast iron containing copper.

A. MANUFACTURE AND STRUCTURE OF COPPER CAST IRON

Inasmuch as copper is less readily oxidized than iron and as its melting point is below that of cast iron, there is no difficulty in alloying small amounts (up to 3 or 4 per cent) with cast iron. A common practice is to add the copper in the form of ingot or scrap to the ladle, but there is no reason why it cannot be added with the charge irrespective of the type of furnace used in melting. Several writers[19,210,224] have suggested that a small amount of aluminum added with the copper insures a better mixing of the copper in the alloy, but the evidence for this is certainly not conclusive. As was pointed out in Chapter III, only a small amount of copper can be dissolved in molten iron-carbon alloys (the solubility depends on the carbon content), but, as evidenced by the manufacture of complex alloys containing 6 or 7 per cent copper, the solubility of copper in cast iron can be increased by the addition of other elements, such as nickel.

One of the most important effects of any alloying element in cast iron is its effect on the tendency to form graphite. In

general, carbide-forming elements, such as chromium and molybdenum, tend to prevent graphite formation, while those elements which do not form stable carbides, such as copper, tend to promote graphite formation. Most workers agree that copper tends to cause graphitization, but some investigators have arrived at the opposite conclusion, as is made evident below. It seems safe to conclude that copper, like silicon, tends to promote graphitization but that its influence is not so pronounced as that of some other elements, aluminum, for example.

128. Effect of Copper on Casting Properties of Iron.—Krilowski[6] found that cast iron containing 0.25 to 2.0 per cent copper possesses good fluidity and fills the mold well. Lipin,[33] in his investigation of cast irons made by adding varying amounts of copper (up to 7 per cent) to Swedish gray iron melted in graphite crucibles, observed that in the same iron, cast at the same temperature, the fluidity increased with rising copper content. However, according to Hamasumi,[142] copper has no appreciable effect on the fluidity of cast iron.

Lipin reported that the density of castings is increased by copper and that the structure of sand-cast iron is uniform, yet, according to Mihailov,[170] copper in amounts not exceeding 1.3 per cent does not affect the density or homogeneity of cast iron.

Little information is available on the effect of copper on shrinkage of castings during solidification though Rolfe[212] gave the result of a shrinkage test made on 12-in. bars of two cast irons, one free from copper, and the other containing 1.3 per cent of copper, the amount of combined and graphitic carbon being approximately the same in both. The shrinkage on 12 in. was 0.19 in. in the copper-free iron, and 0.179 in. in the iron with 1.3 per cent copper.

Lipin[33] claimed that the thickness of chill on iron cast into iron molds increased with increasing copper content. However, Rolfe[212] reported that 1.3 per cent copper decreased the depth of chill from 0.65 to 0.37 in. Spencer and Walding[335] observed practically no effect of copper on the depth of chill.

Recently Taniguchi[337] investigated the effect of copper and other elements on the depth of chill of cast-iron rolls containing 3.11 per cent carbon, 0.58 per cent silicon, and 0.57 per cent manganese. The alloys were cast in an iron mold, 5.12 × 2.76 × 3.94 in., from 1280°C. (2335°F.) after holding at 1500°C.

(2730°F.) for 15 min. The surface hardness of these chilled specimens was tested by a scleroscope. The depth of chill was found first to decrease as the copper content was increased to about 4 per cent, and to increase on further addition of copper.

129. Influence of Copper on Graphite Formation.—The evidence available in the literature on the effect of copper on graphite formation in cast iron during solidification is somewhat contradictory. Stead[39] failed to observe any influence of copper in retaining the carbon in the combined form or in causing the separation of graphite. Boegehold, in U. S. Patent 1,707,753, April 2, 1929, claimed that copper retards the graphitization during solidification.

On the other hand, the majority of investigators agree that the effect of copper is to promote graphitization. Smalley,[132] Rolfe,[212] Pfannenschmidt,[243] and Hurst[320] noted a tendency for the combined carbon content of cast iron to decrease with the addition of copper. Hotari,[204] from microscopic and chemical analyses of a cast iron containing 3.4 per cent total carbon, 1.5 per cent silicon, and nil to 1.7 per cent copper, concluded that copper increases the amount of graphite.

Lorig and MacLaren also observed the effect of copper in promoting graphitization, as is shown by Table 62.

TABLE 62.—EFFECT OF COPPER ON GRAPHITIZATION*

Heat number	Carbon, per cent			Other elements, per cent				
	Total	Combined	Graphitic	Si	Mn	Cu	S	P
111	2.47	1.64	0.83	1.41	0.73	0.0	0.02	0.095
111	2.44	1.39	1.05	1.41	0.73	1.1	0.02	0.095
112	3.18	0.68	2.50	1.66	0.86	0.0	0.02	0.104
112	3.15	0.57	2.58	1.66	0.86	0.74	0.02	0.104
112	3.10	0.65	2.45	1.66	0.86	1.79	0.02	0.104

* Lorig and MacLaren (unpublished investigation).

The cast iron was melted without copper; all additions of this element were made to the ladle. It may be observed from the table that the addition of 1.10 per cent copper lowered the percentage of combined carbon 0.25 per cent, which indicates that graphitization is accelerated by copper. Further confirmation of this action of copper was noted in the decreased combined

carbon content of heat 112 by the addition of 0.74 per cent copper. As seen from the table, the effect of copper is more pronounced in heat 111, which contained lower total carbon and silicon.

Lorig and MacLaren also determined the influence of copper on the graphitizing tendency of irons of compositions corresponding to cupola malleable iron. Stepped bars containing different

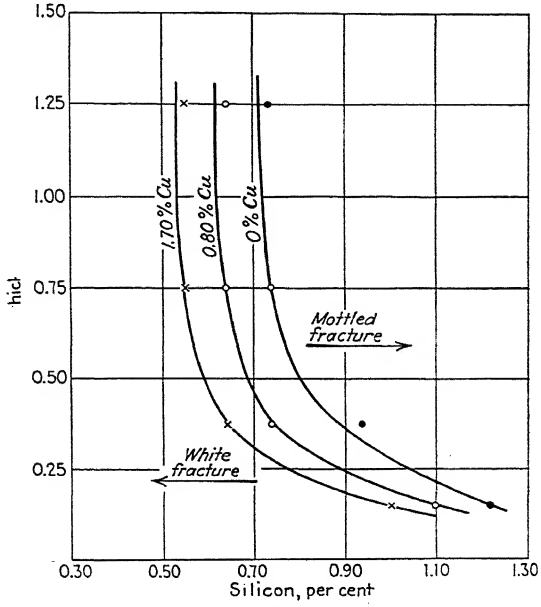


FIG. 128.—Relation of section size, silicon content, and copper content to formation of graphite in hard-iron castings. (*Lorig and MacLaren.*)

amounts of silicon and copper were prepared from two heats of iron containing respectively 2.8 and 2.9 per cent carbon. The bars were fractured and the fractures examined to determine whether or not graphite had formed. The results of the observations are given in Fig. 128, which shows that copper does tend to promote graphitization and that the addition of 1 per cent copper to the iron is equivalent to increasing the silicon content by 0.1 or 0.2 per cent in so far as graphitization is concerned.

Hamasumi[142] observed no accelerating effect of copper on graphitization of cast iron containing about 3 per cent total

carbon, when 1.8 per cent silicon was present. It is probable that in high-silicon irons the effect of copper is obscured by the silicon which is a stronger graphitizing agent than copper.

130. Effect of Copper on Distribution, Size, and Form of Graphite.—Smalley[132] noted that in a cast iron containing 5 per cent copper the graphite was present in well-distributed fine flakes. He reported that copper breaks up the flakes of graphite and imparts toughness to cast iron. This was confirmed by Hamasumi.[142] Mihailov[170] noted that in cast irons with a hypereutectoid matrix the presence of copper manifested itself by decrease in the quantity of free cementite and by refinement of the separated graphite.

Contrary to this, Rolfe[212] observed microscopically an increase in size of graphite flakes when 1.3 per cent copper was added to a cast iron containing 3.7 per cent total carbon and 1 per cent silicon.

In a study of silicon-free alloys von Keil and Ebert[355] found that copper decreased the carbon content necessary for the stable eutectic to form on solidification when the alloys were cooled at the rate of 30°C. (55°F.) per min. Its influence was of the same order as that of nickel and not nearly so great as that of aluminum.

Krilowski[6] observed that the fracture of cast iron containing 0.25 to 2 per cent copper is bright and lamellar, and after slow cooling dull and finely granular. Lipin[33] reported that the dark-gray earthy fracture of Swedish gray cast iron became lighter and the grain coarser as the copper content increased. With 0.8 per cent copper the core was coarse grained, light, and shiny, and the outer portions had a dark earthy structure. With 2 per cent copper the whole cross-section of the casting consisted of coarse shiny grains.

131. Influence of Copper on Structure of the Matrix.—No evidence has been found that copper influences the structure of the matrix in gray cast iron. The structure is, of course, dependent on the amount of combined carbon, and copper has some tendency to decrease the amount of combined carbon and thus to affect indirectly the structure of the matrix. For a given content of combined carbon there is no reason to expect the structure of the matrix of a copper iron to differ from that of an unalloyed iron.

B. INFLUENCE OF COPPER ON THE PROPERTIES OF CAST IRON

The mechanical properties of cast iron depend on the constitution of the matrix and on the form and amount of graphite. Large flakes of graphite, forming a more or less continuous network, break the continuity of the metal and decrease the strength. Graphite particles when broken up or rounded do not produce so much discontinuity in the matrix and, therefore, exert a less injurious influence on the strength of the metal.

The properties of the matrix depend on the amount of dissolved copper and the amount of combined carbon. In comparing the properties of irons containing various amounts of copper the amount of combined carbon should be taken into account. As was mentioned before, the manufacturing procedure may greatly influence the changes in properties when copper is added. For these reasons the results obtained by various investigators are not strictly comparable; hence the more important investigations are here taken up separately.

132. Mechanical Properties.—One of the earlier quantitative studies of the effect of copper on the strength of cast iron was made by Lipin, in 1895.[33] Copper-bearing gray irons were prepared by melting Swedish gray iron and copper in graphite crucibles (25-kg. charges) and pouring in sand. The chemical composition and the results of tensile tests together with the observations on casting properties are given in Table 63. Although the results are not exactly comparable because of large variations in the combined carbon content, they indicate a general trend of the tensile strength to increase with rising copper content.

The work of Smalley[132] gave some indications of increased hardness and improved transverse strength when copper in amounts from 5 to 10 per cent was added to a hematite pig iron containing 3.3 per cent total carbon, 2 per cent silicon, and 0.7 per cent manganese.

An investigation of Hamasumi[142] showed that the strength of cast iron is considerably increased by an addition of copper up to 1 per cent. Further addition of copper did not materially affect the strength, but the hardness gradually increased with the copper content. The machinability was not affected by copper. The chemical compositions and the results of tests are given in Table 64.

TABLE 63.—PROPERTIES OF COPPER CAST IRON*

Composition, per cent							Tensile strength,† lb. per sq. in.	Fracture of sand-cast specimens
Graph-	Total carbon		Mn		Cu			
2.94	3.24	1.46	0.57	0.095	0.020	0.0	42,100	Dark gray, very fine, earthy
2.74	3.38	1.32	0.66	0.082	0.016	0.0	42,700	Same
3.14	3.71	.....	.....	.....	.....	0.27	45,800	Same
2.97	3.23	1.53	0.82	0.088	0.017	0.29	46,800	Same, but somewhat lighter
2.63	3.55	.....	.....	.....	.....	0.48	42,700	Same, in the middle of specimen coarse grained and shiny
2.13	3.25	1.22	0.61	.	0.022	0.86	43,500	Same
2.13						1.0	45,300	Same
3.04	3.15	2.00(?)	0.70		0.016	1.09	42,100	Same
3.15	3.66	1.55	0.62	.	0.015	1.22	43,000	Same
3.14	3.57	1.49	0.76	.	0.016	1.53	43,200	More shiny, conchoidal fracture
3.19	3.41	1.47	0.56		0.011	1.94	43,400	Entire fracture shiny, only dull and earthy on edges
3.19						2.70	46,200	Entire fracture lighter and coarser of grain
3.10	3.55					3.23	43,500	Coarse, light-gray shiny grains
3.45	3.66					3.98	46,100	Same
2.85	3.53	0.93	0.52	0.086	.....	4.90	49,800	Same

* Lipin.[33]

† Average of two to four tests.

The beneficial effect of copper on the strength, hardness, and bending properties of cast iron was confirmed by Pfannenschmidt,[243] Hotari,[204] Skorčelletti and Šultin,[304] and Lorig and MacLaren, but Rolfe[212] found that a gray iron containing 1.3 per cent copper had a lower transverse strength and a lower tensile strength than a copper-free iron.

Taniguchi[337] showed that the scleroscope hardness of the chilled layer of cast iron containing 3.11 per cent carbon, 0.58 per cent silicon, and 0.57 per cent manganese increased slightly as the copper content increased up to 1.5 per cent; further addition of copper caused a slight and gradual decrease in hardness.

Tests made by Hurst[320] on cylindrical cast-iron drums cast by the centrifugal process in metal molds showed no appreciable effect of copper on mechanical properties. As Table 65 indicates, the breaking strength of the cast iron decreased slightly with the increase of copper up to 2 per cent, with a recovery to the original value in the 3 per cent copper sample. The permanent-set

TABLE 64.—EFFECT OF COPPER ON MECHANICAL PROPERTIES OF GRAY CAST IRON*

Composition, per cent					Tensile strength,† lb. per sq. in.	Brinell hardness	Machinability
Total C	Graphite	Combined C	Si	Cu			
Casting temperature 1350°C. (2460°F.)							
2.96	2.13	0.83	1.79	0.25	39,700	187	Very soft
2.81	2.08	0.73	1.79	0.33	44,600	206	Very soft
3.11	2.20	0.91	1.85	0.45	45,600	196	Very soft
3.01	2.20	0.81	1.74	0.65	46,700	196	Very soft
2.98	2.18	0.80	1.77	0.91	47,200	229	Soft
2.99	2.25	0.74	1.81	1.09	46,700	216	Soft
2.85	2.19	0.66	1.83	1.49	44,900	215	Good
2.92	2.15	0.77	1.88	2.11	45,400	219	Good
2.73	1.94	0.79	1.82	2.20	46,400	233	Good
2.94	2.29	0.65	1.85	3.34	44,300	230	Somewhat hard
3.05	2.07	0.98	1.83	3.88	43,700	248	Somewhat hard
Casting temperature 1400°C. (2550°F.)							
2.89	2.08	0.81	1.89	0.23	44,500	199	Soft
2.87	2.01	0.86	1.80	0.45	45,600	204	Soft
2.92	2.13	0.79	1.78	0.66	47,300	217	Soft
2.98	2.18	0.80	1.79	0.84	47,400	222	Good
2.95	2.02	0.93	1.72	1.15	49,100	207	Good
2.99	2.16	0.83	1.74	1.56	47,500	217	Good
2.87	2.04	0.83	1.75	2.10	47,700	241	Good
2.92	2.09	0.83	1.73	2.64	48,200	229	Good
3.07	2.25	0.82	1.72	2.80	50,100	249	Good
2.84	2.16	0.68	1.78	3.79	50,900	241	Good

* Hamasumi.[142]

† Average of two tests.

value was practically unaffected in all but the 3 per cent sample in which it was considerably lowered. Except for the last sample the Brinell hardness was found to be lowered by the addition of copper. Stress-deflection curves contained no peculiarities which could be attributed to the presence of copper. These results showed that copper in amounts from nil to 3 per cent had no influence in either increasing or decreasing the brittleness of this particular lot of cast iron.

TABLE 65.—EFFECT OF COPPER ON MECHANICAL PROPERTIES OF CAST IRON*

Sample number	Composition, per cent							Modulus of elasticity, lb. per sq. in., $\times 10^{-6}$	Tensile strength, lb. per sq. in.	Modulus of rupture, lb. per sq. in.	Permanent set, per cent	Brinell hardness
	Total C	Graphite	Si	P	S	Mn	Cu					
1	3.26	2.56	2.10	....	0.098	0.76	Nil	17.0	44,600	71,500	9.2	248
2	3.24	2.54	2.07	....	0.098	0.76	0.70	16.9	44,100	70,800	9.4	243
3	3.25	2.59	2.07	....	0.098	0.76	1.41	16.7	41,700	66,700	10.2	227
4	3.22	2.54	2.07	0.71	0.098	0.76	1.81	17.0	41,900	66,900	9.8	230
5	3.24	2.59	1.97	0.71	0.098	0.76	3.06	17.1	44,600	71,500	7.0	254

* Hurst.[320]

TABLE 66.—TRANSVERSE TESTS OF COPPER CAST IRON*

Total carbon, per cent	Copper, per cent	Transverse breaking load, lb.†			Deflection, in.†		
		As cast	Reheated at 500°C. (930°F.) for 3 hr.	Increase in load due to reheating	As cast	Reheated at 500°C. (930°F.) for 3 hr.	Increase in deflection due to reheating
3.18	0.0	4040	4250	.....	0.102	0.118	
3.18	0.0	3870	3360	.....	0.100	0.100	
3.18	0.0	Av. 3955	3805	−150‡	0.106	0.109	+0.008
3.15	0.74	4100	3800	.....	0.110	0.105	
3.15	0.74	4280	3610	.....	0.116	0.098	
3.15	0.74	Av. 4190	3705	−485‡	0.113	0.103	−0.010‡
3.10	1.79	4620	4170	.....	0.115	0.117	
3.10	1.79	3830	3880	.....	0.090	0.102	−0.010‡
3.10	1.79	Av. 4225	4025	−200‡	0.102	0.109	+0.007

* Lorig and MacLaren.
† 1.2-in. diameter bars, 12-in. span.
‡ Decrease.

In a recent article Hurst[395] concluded that, in general, copper in cast iron exercises an influence similar to that of nickel and that its greatest potential use in cast iron is as a diluent of the more expensive nickel.

Eddy[389] recently claimed that he had found that copper greatly improves the properties of gray iron, but he gave no test results.

The influence of copper on the wear resistance of cast iron containing 3 per cent carbon and 2.3 per cent silicon was studied by Söhnchen and Piwowarsky.[379] The samples contained from 0.5 to 2 per cent copper. Tests on a laboratory machine indicated that increasing the copper content from 0.5 to 2 per cent did not affect the wear loss with rolling friction, but comparison with other results indicated that 0.5 per cent copper increased the wear resistance. With sliding friction wear resistance increased as the copper content increased.

TABLE 67.—TENSILE STRENGTH AND BRINELL HARDNESS OF COPPER CAST IRON*

Total carbon, per cent	Copper, per cent	Tensile strength, lb. per sq. in.			Brinell hardness		
		As cast	Reheated at 500°C. (930°F.) for 3 hr.	Increase in strength due to reheating	As cast	Reheated at 500°C. (930°F.) for 3 hr.	Increase in hardness due to reheating
3.18	0.0	35,650	36,500				
3.18	0.0	36,500	36,250	.....	197	197	
3.18	0.0	37,700	35,500	.....	198	197	
3.18	0.0	37,200	34,870				
		Av. 36,760	35,780	−980†	198	197	−1†
3.15	0.74	37,250	40,750				
3.15	0.74	36,500	41,000	.....	211	218	
3.15	0.74	38,000	40,500	.....	210	220	
3.15	0.74	.....	39,000				
		Av. 37,250	40,310	+3,060	211	219	+9
3.10	1.79	39,850	41,500				
3.10	1.79	39,000	42,000	.....	231	225	
3.10	1.79	42,500	41,800	.....	218	228	
3.10	1.79	41,500	40,370				
		Av. 40,710	41,420	+710	225	227	+2

* Lorig and MacLaren.
† Decrease.

133. Effect of Precipitation Treatment on Copper Cast Iron.—In spite of the fact that copper increases the strength and hardness of cast iron, it apparently does not render cast iron susceptible to precipitation hardening. This conclusion was reached by Lorig and MacLaren and was based on the results of tests on samples of heat 112 whose chemical composition and preparation were described on page 272. Samples were tested for transverse strength, deflection, Brinell hardness, and tensile strength, both in the as-cast condition and after they had been given a precipitation-hardening treatment which consisted of reheating the bars to 500°C. (930°F.) for 3 hr. The transverse tests were made on 1.2-in. diameter bars over a span of 12 in.

As may be noted from the results shown in Tables 66 and 67, some improvement with copper content occurred in the transverse strength, the tensile strength, and the Brinell hardness.

The results of the precipitation-hardening treatment were interpreted by Lorig and MacLaren as follows:

A prolonged heating at 500°C. (930°F.), a treatment simulating the precipitation-hardening treatment for copper-containing steels, had no material influence on the mechanical properties. All transverse strength values were slightly depressed, the total deflection values and the Brinell hardness values remained practically unchanged, and the tensile strength values of the bars containing copper were raised. In view of the fact that heating to approximately 500°C. (930°F.) for several hours is sometimes resorted to commercially to relieve casting strains in gray iron castings, and that slight increases in tensile strength without alterations in Brinell hardness values have been reported from such treatment,[307] the change in tensile strength which we have noticed in the copper cast iron by a similar treatment cannot be definitely attributed to the precipitation-hardening effect of the copper. Under the circumstances, no worthwhile benefit to mechanical properties can be assured from the precipitation-hardening effects of copper in cast iron of the type used in the above experiments. This cast iron is pearlitic. There is some probability that a cast iron more ferritic in structure would respond to the treatment to a greater extent.

As will be shown later, the mechanical properties of copper-containing malleable cast iron are improved by the precipitation-hardening treatment.

134. Effect of Copper on the Corrosion and Acid Resistance of Cast Iron.—Very little information is found in the literature on the influence of copper on the corrosion resistance of cast iron. Most of the data refer to laboratory tests by immersion in solutions of various acids or salts, which may or may not bear any relation to the behavior of iron under actual service conditions.

Comparative solution tests indicate that the solution rate in hydrochloric and sulphuric acids is considerably decreased by copper. This has been noted by Mihailov,[170] Hotari,[204] Kötzschke and Piwowarsky,[209] and others.

Denecke[198] made solution tests in 10 per cent hydrochloric acid of gray iron containing 4.15 per cent total carbon, 1.29 per cent silicon, 0.26 per cent manganese, and copper varying from nil to 1.5 per cent in 0.25 per cent steps. In all cases addition of copper increased the resistance of cast iron to acid attack. The resistance was somewhat lowered by annealing for 30 min. at 800°C. (1470°F.), although in all cases the copper irons were superior to the irons containing no copper. The maximum resist-

ance was attained with about 0.5 per cent copper; further additions of copper did not seem to affect the solution rate to any appreciable extent.

Pfannenschmidt[243] made corrosion tests in molten potassium hydroxide, sodium hydroxide, and 10 per cent solutions of hydrochloric and sulphuric acids. The results are in agreement with those of Denecke. Copper was found to increase the resistance in 1 per cent acetic and, to a smaller extent, in 1 per cent sulphuric acid. Table 68 shows some results of corrosion tests[243] in mine water for specimens alternately submerged and exposed. It appears that even small additions of copper (0.18 per cent) improve the resistance of cast iron to the attack by mine water.

TABLE 68.—EFFECT OF COPPER ON THE RESISTANCE OF GRAY CAST IRON TO CORROSION IN MINE WATER*

Composition, per cent					Duration of test, hr.	Loss in weight, mg. per sq. cm.	Duration of test, hr.	Loss in weight, mg. per sq. cm.
C	Si	Mn	P	Cu				
3.18	1.86	0.94	0.29	0.0	550	20.2	1100	33.0
3.16	1.86	0.94	0.29	0.18	550	14.8	1100	18.0
3.10	1.86	0.84	0.25	0.0	550	18.4	1100	26.3
3.00	1.86	0.84	0.25	1.26	550	15.0	1100	16.5
3.31	1.79	0.93	0.37	0.0	550	19.7	1100	30.3
3.28	1.79	0.93	0.37	0.87	550	16.8	1100	18.0

* Pfannenschmidt.[243]

Hotari[204] made tests on nine types of cupriferous cast irons containing 3.4 per cent total carbon, 1.5 per cent silicon, and nil to 1.7 per cent copper. The tests were made by immersing the samples in 5 per cent solutions of hydrochloric, nitric, and sulphuric acids, and in solutions of sodium chloride and sodium hydroxide for 48 hr. The results showed that the copper markedly increased the resistance to acid attack, the maximum effect being obtained by adding 0.25 per cent copper.

Kötzschke and Piwowarsky[209] made corrosion tests in an "artificial damp atmosphere" produced by a salt spray (without, however, the drops touching the specimens) and in the outdoor atmosphere. The specimens were kept for 5 days in the spray and 28 days in the atmosphere. The results showed that 0.3 to 0.4 per cent copper reduced the atmospheric corrosion about

25 per cent. Higher copper content brought no further improvement. The action of copper, it was concluded, depends on the formation of a dense, adherent rust layer which protects the metal from further attack.

According to a private communication from J. T. MacKenzie of the American Cast Iron Pipe Company:

> Large tonnages of cast-iron pipe containing approximately 1 per cent copper have been used for the last decade for condenser coils, in crude gasoline stills. While in some installations the value has been small, yet in a few cases the life was as much as five times that of plain cast iron. At present we are not able to predict the effect of copper, as it varies with the different crude oils.

135. Effect of Copper on the Growth of Cast Iron.—Bauer and Sieglerschmidt[227] studied the effect of small additions of copper and nickel on the expansion and growth of cast iron by means of dilatometric measurements. Three 4 × 5 × 10-cm. (1.6 × 2.0 × 3.9-in.) test pieces of the following composition were cast in sand:

	Composition, per cent				
	C	Si	S	Cu	Ni
A	3.15	1.12	0.114		
B	3.15	1 12	0.114	0.55	
C	3.15	1.12	0.114	....	0.48

It was found that the expansion of cast iron was not appreciably influenced by small additions of copper or nickel in the temperature interval from 20 to 670°C. (70 to 1240°F.) since no structural changes due to decomposition of carbides occur. However, when the carbides disintegrate, a permanent deformation takes place. Specimen *A*, without additions, showed the greatest residual expansion on cooling to room temperature (0.201 per cent). Iron *B* with 0.55 per cent copper, expanded 0.155 per cent and the nickel-bearing iron 0.153 per cent. The investigators concluded that small quantities of copper and nickel retard the formation of graphite on heating; it may be, however, that the difference arose from the difference in combined carbon content and not from the greater stability of the cementite in these alloy irons.

C. COPPER IN MALLEABLE CAST IRON

Malleable cast iron rarely contains alloying elements, although copper has recently been used in commercial castings of this material. The copper irons that have been produced have contained in the neighborhood of 0.5 per cent copper, and the copper was added to improve corrosion resistance and/or to increase strength. Miss Hall,[352] however, in a recent article stated that copper apparently has little influence on malleable iron.

One of the most important considerations regarding the influence of an alloying element in malleable cast iron is how the element affects graphitization, for the alloy must cast as white iron, and all of the combined carbon (in American practice) must be converted into graphite by an annealing treatment. Evidence that 1 per cent copper in cast iron has an influence on graphitization on casting comparable to that produced by increasing the silicon content by 0.1 or 0.2 per cent was presented earlier in this chapter. This would indicate that when copper is added to malleable iron the silicon content must be decreased by 0.1 or 0.2 per cent for each per cent of copper added, in order to prevent mottling—the partial decomposition of cementite in the castings. The influence of copper on graphitization during annealing will be considered below, as well as the influence of copper on the properties of the iron.

136. Influence of Copper on Malleableizing.—In a typical malleableizing treatment, according to a recent symposium,[275] the castings of white iron are heated at such a rate that they reach the annealing temperature of 845 or 870°C. (1550 or 1600°F.) in about two days. They are held at the annealing temperature for 48 to 60 hr., then cooled at a rate of not more than 4.5 or 5.5°C. (8 or 10°F.) per hr. to a temperature in the neighborhood of 690°C. (1275°F.), after which they may be cooled comparatively rapidly. The long time at the annealing temperature is necessary in order to decompose the cementite that is present with austenite at that temperature, and the slow cooling through the critical range is necessary in order to decompose the cementite in the pearlite formed on cooling through the lower critical temperature. Some laboratory tests described below indicate that copper tends to promote graphite formation in the annealing process and that copper permits a shortening of malleableizing time. Confirmatory evidence from actual plant operation is, however, lacking.

In determining the influence of a number of elements on the graphitization of white iron on annealing, Sawamura[243] made dilatometric studies on alloy irons heated at the rate of 5°C. (9°F.) per min. The results indicated that copper lowered the temperature at which graphitization began on heating, copper having practically the same effect as nickel.

To ascertain the effect of copper on the speed of graphitization, Smith and Palmer* traced microscopically the disappearance of cementite by examining samples after heating for various periods of time at 925°C. (1695°F.). Before heating, the samples had the following composition (percentage):

Material	Total carbon	Graphite	Silicon	Copper
Copper-free iron	2.32	none	1.21	0.0
Copper-containing iron	2.32	none	1.22	0.98

The specimens were in the form of disks, 0.5 in. thick, cut from 0.75-in. cast rods. At the end of 4 hr. at 925°C. (1695°F.) the copper-free metal still contained an appreciable amount of cementite while in the copper-containing metal only a few traces were present. After 6 hr. both metals were quite free from cementite. Typical structures are shown in Figs. 129 to 132. The structures of the two castings before heating were identical. As may be seen by comparing Figs. 129 and 130, the amount of cementite remaining after heating for 2 hr. is much less in the casting containing copper than in the other. These specimens were etched with boiling sodium picrate which stains the cementite network brown (photographed black), while ferrite remains white, pearlite gray, and the black graphite nodules are unaffected. The difference in appearance is still more strikingly illustrated in Figs. 131 and 132, representing the structures of the same alloys which had been heated at 720°C. (1330°F.) for 4 hr. after a treatment to graphitize all the undissolved cementite. It may be seen that the casting containing 1 per cent copper was completely malleableized, while the copper-free casting still contained some pearlite.

* Unpublished reports made available through the courtesy of the Copper and Brass Research Association.

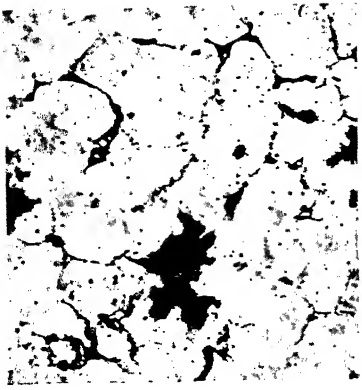


FIG. 129.—White cast iron, 1.2 per cent silicon and no copper, annealed 2 hr. at 925°C. (1695°F.), air cooled. Etched with sodium picrate. 200×. (*Smith and Palmer.*)

FIG. 130.—White cast iron, 1.2 per cent silicon and 1.0 per cent copper. Same treatment as in Fig. 129. Etched with sodium picrate. 200×. (*Smith and Palmer.*)

FIG. 131.—White cast iron, 1.2 per cent silicon and no copper, annealed 8 hr. at 925°C. (1695°F.), cooled to 760°C. (1400°F.) in 12 hr., held 4 hr. at 720°C. (1330°F.). Etched with nitric acid in alcohol. 200×. (*Smith and Palmer.*)

FIG. 132.—White cast iron, 1.2 per cent silicon and 1.0 per cent copper. Same treatment as in Fig. 131. Etched with nitric acid in alcohol. 200×. (*Smith and Palmer.*)

In order to obtain the shortest possible annealing cycle, samples of the two alloys were subjected to a treatment consisting of heating for 6 hr. at 925°C. (1695°F.), cooling in 8 hr. to 760°C. (1400°F.), and holding 8 hr. at 720°C. (1330°F.). This cycle was not sufficient to malleableize the copper-free iron, but the copper-containing iron was completely malleableized. The entire cycle from charging in the hot furnace to the end occupied only 24 hr., which is a remarkably short time for complete malleableization.

In determining the influence of copper on the rate of graphitizing of white iron of the type used for malleableization, Smith and Palmer made dilatometric measurements with a dilatometer of special construction in which the gage indicating change in length and a watch were photographed at regular intervals by a moving-picture camera. The curves permitted an estimation of the amount of graphitization at any instant during heating or while at the malleableizing temperature. From the dilatometric curves and from microscopic examination it was found that copper influenced the graphitizing time for commercial irons in the manner shown in Table 69, where it will be seen that 1.33 per cent copper reduces the malleableizing time by about 50 per cent.

TABLE 69.—TIMES FOR FIRST- AND SECOND-STAGE GRAPHITIZATION FOR SIX COMMERCIAL MALLEABLE CAST IRONS*

Mark	Composition, per cent		Time for	
	Copper	Silicon	First stage at 925°C. (1695°F.)	Second stage at 725°C. (1335°F.)
*A*1	0.0	1.01	8 hr. 0 min.	13 hr. 10 min.
*A*2	1.33	1.01	5 hr. 10 min.	6 hr. 0 min.
*A*3	1.73	1.01	4 hr. 0 min.	5 hr. 30 min.
*A*4	2.94	1.01	2 hr. 25 min.	4 hr. 30 min.
*B*1	0.05	0.91	12 hr. 5 min.	18 hr. 20 min.
*B*2	1.22	0.91	5 hr. 40 min.	8 hr. 10 min.

* Smith and Palmer (unpublished work).

Lykken[364] made a similar study, in which his specimens were placed in iron-pipe containers surrounded with granular carbon, heated in an automatically controlled Hump furnace, and finally cooled in the pipe containers.

In order to determine the time needed to decompose the massive Fe_3C, the "white-fracture" samples were placed in the furnace maintained at 925 ± 5°C. (1700 ± 10°F.). After the samples had been heated the required time, the charge was cooled in the furnace to 790°C. (1450°F.) for 1 hr. before removing. The progress of the heat treatment was determined by examining the polished section for Fe_3C after etching with alkaline sodium picrate.

A similar treatment was used to determine the time necessary to complete the graphitization of the austenite. Fresh samples were heated 10 hr. at 925°C. (1700°F.) and then cooled to 790°C. (1450°F.) at a rate of 30°C. (50°F.) per hr. The furnace was then cooled from 790 to 690°C. (1450 to 1275°F.) in 10 min. The samples were then maintained at 690 ± 5°C. (1275 ± 10°F.) for some time while a sample-container was taken out every hour. A polished section was examined for the presence of pearlite, after etching with 5 per cent alcoholic nitric acid.

Reviewing the data, one finds that the times for the secondary stage are unusually short. However, photomicrographs show that the samples were completely graphitized in the indicated time. The writer has no definite explanation for these abnormal results.

Two per cent copper shortens the total annealing time about 22 per cent: copper accelerates both stages of the graphitization equally. Above 2 per cent of copper, there is no further effect on either stage. Carbon and silicon have the same influence in copper-bearing castings as in ordinary white cast iron. Gray castings were produced with 3.28 per cent carbon and 0.85 per cent silicon and with 2.58 per cent carbon and 1.15 per cent silicon in the presence of 1 per cent copper.

The presence of copper does not markedly influence the structure of the white cast iron. However copper tends to refine the grain of the malleableized castings. The ferrite and pearlite of copper-bearing castings seem to etch much faster than the pure constituents.

The results are shown in Table 70. Besides the elements shown in the table, the specimens contained 0.03 to 0.04 per cent sulphur, 0.22 to 0.26 per cent manganese, and 0.11 to 0.14 per cent phosphorus.

137. Special Heat Treatments for Malleable Iron Containing Copper.—If copper malleable iron is to be given a precipitation-hardening treatment, attention must be given to the behavior of the carbon as well as that of the copper. In order to obtain copper in a supersaturated solution, it is necessary to cool fairly rapidly (air cool) from a sufficiently high temperature, but the temperature must be below that at which austenite is stable, or an appreciable quantity of carbon will be dissolved and the

TABLE 70.—TIMES FOR FIRST- AND SECOND-STAGE GRAPHITIZATION FOR 18 IRONS*

Alloy number	Composition, per cent			Fracture of casting	Time for decomposition of massive cementite at 925°C. (1700°F.), hr.	Time for graphitization of eutectoid carbide at 690°C. (1275°F.), hr.
	Cu	C	Si			
11	4.47	2.33	0.81	White	6	3
12	3.10	2.52	0.84	White	5	3
13	2.26	2.49	0.81	White	5	3
14	1.94	2.54	0.81	White	5	3
15	1.35	2.52	0.82	White	6	3
37	1.03	2.60	0.85	White	7	4
17	0.76	2.59	0.85	White	7	4
18	0.60	2.60	0.84	White	7	4
19	0.40	2.60	0.84	White	7	4
20	0.17	2.60	0.87	White	8	5
21	0.01	2.63	0.84	White	8	4
22	0.92	2.84	0.84	White	6	3
23	0.92	3.08	0.82	Mottled	5	3
26	0.91	2.71	0.95	Mottled	6	4
27	0.94	2.61	1.07	Mottled	5	4
30	0.94	2.08	0.83	White	7	8
31	0.92	2.50	0.68	White	7	6
R	0.00	2.51	0.88	White	8	5

* Lykken.[364]

matrix of the iron will be a high-carbon steel instead of ferrite. Studies by Smith and Palmer showed that 735°C. (1355°F.) is the lowest temperature at which sufficient copper is dissolved to render the castings precipitation hardenable and that at 745°C. (1375°F.), for one iron, the temper carbon began to go into solution.

Some interesting observations were made regarding the influence of copper on the critical points of malleable cast iron. In the presence of 0.9 per cent silicon, addition of 1 per cent copper caused the lowering of the critical point (microscopically determined) from 756 to 738°C. (1385 to 1360°F.), but further additions of copper had no effect on the critical points. In iron containing 1.2 per cent silicon and no copper the critical point was observed at 760°C. (1400°F.) and was steadily depressed to 748°C. (1380°F.) when the copper content was raised to 2 per cent (Table 71).

TABLE 71.—INFLUENCE OF COPPER ON THE CRITICAL POINTS OF MALLEABLE IRON*

Composition, per cent			Critical temperature	
C	Si	Cu	°C.	°F.
2.36	0.89	0.03	756	1395
2.34	0.96	0.67	748	1380
2.27	0.82	1.06	738	1360
2.28	0.99	1.52	737	1360
2.27	0.99	1.97	737	1360
2.30	0.97	3.02	737	1360
2.20	1.19	0.05	760	1400
2.27	1.27	0.67	755	1390
2.27	1.23	1.04	752	1385
2.28	1.19	1.53	750	1380
2.29	1.18	2.01	748	1380
2.37	1.19	2.06	748	1380
2.04	1.25	0.00	762	1405
2.06	1.23	1.04	748	1380
2.09	1.21	2.07	748	1380
2.05	0.96	0.07	756	1395
2.07	0.98	1.01	747	1375
2.12	0.94	2.03	738	1360
2.84	0.97	0.04	760	1400
2.78	0.95	1.03	735	1355
2.70	0.90	2.12	735	1355

* Smith and Palmer (unpublished work).

Lykken[364] determined thermal critical points on malleable iron of 2.05 per cent carbon, 0.65 per cent silicon, 0.21 per cent manganese, 0.031 per cent sulphur, and 0.141 per cent phosphorus, with copper as shown in Table 72. He used the differential method, employing a Leeds and Northrup apparatus. Heating and cooling rates were about 10°C. (18°F.) per min. The specimens were annealed before taking the thermal curves.

138. Mechanical Properties of Precipitation-hardened Malleable Iron.—Figure 133, from Smith and Palmer, shows the properties of laboratory-cast samples of malleable iron containing 1 per cent copper after having been normalized from different temperatures and then given a precipitation-hardening treat-

TABLE 72.—THERMAL CRITICAL POINTS OF COPPER-BEARING MALLEABLE IRON*

Sample number	Copper, per cent	Thermal values			
		Cooling		Heating	
		°C.	°F.	°C.	°F.
10	0.04	740	1365	760	1400
8	0.39	730	1345	760	1400
7	0.50	730	1345	760	1400
6	0.72	725	1335	755	1390
6	0.72	730	1345	760	1400
4	0.94	720	1330	755	1390
3	1.46	710	1310	750	1380
1	3.00	700	1290	750	1380

*Lykken.[364]

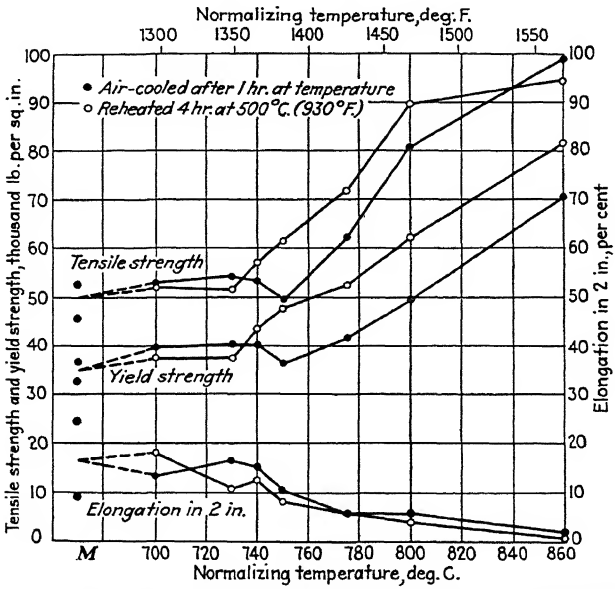


FIG. 133.—Properties of malleable iron containing 2.2 per cent carbon, 1.0 per cent silicon, and 1.0 per cent copper, normalized as indicated and reheated to 500°C. (930°F.). (*Smith and Palmer.*)

ment. As the normalizing temperature exceeded 750°C. (1380°F.) the strength increased appreciably, but the ductility

TABLE 73.—MECHANICAL PROPERTIES OF HEAT-TREATED MALLEABLE CAST IRON CONTAINING COPPER*

Composition, per cent					Mechanical properties, heated 1 hr. at 735 to 745°C. (1355 to 1375°F.)			Mechanical properties, heated 1 hr. at 735 to 745°C. (1355 to 1375°F.), reheated 3 hr. at 500°C. (930°F.)		
C	Si	Mn	P	Cu	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent
2.36	0.94	0.27	0.132	0.031	62,500 64,000	42,500 45,500	18.0 17.5	61,000 63,000‡	41,000 41,000	15.5 17.0
2.31	1.08	0.22	0.109	0.63	61,000 61,000	45,500 45,500	23.5 24.0	60,500 42,500§	44,000	24.5 3.5
2.27	1.11	0.22	0.106	1.12	61,500† 60,000	48,000 48,000	15.5 13.5	63,000 65,500	50,000 51,000	13.5 20.5
2.38	1.13	0.28	0.128	1.30	60,000 60,500	47,500 48,000	15.0 16.5	65,000 66,000	53,500 55,000	13.0 15.0
2.36	1.10	0.26	0.124	1.50	61,000 61,500	49,500 51,000	18.5 17.5	64,500 66,500	52,500 55,500	17.0 13.5
2.33	1.11	0.27	0.122	2.01	62,000 62,000	50,500 49,000	19.0 18.0	70,500 69,000	59,000 58,500	17.0 11.0
2.34	1.04	0.26	0.119	2.68	60,500 62,000	49,000 49,000	17.0 16.0	65,000 66,500‖	56,000 59,500	12.5 5.5
2.29	1.19	0.25	0.105	0.60	59,000 59,500	45,000 44,500	23.5 22.0	60,500 59,500	45,000 44,000	22.5 23.0
2.31	1.22	0.25	0.110	1.00	62,000 62,000	49,000 50,000	20.0 17.0	67,000 68,000	55,500 55,000	12.0 21.0
2.36	1.29	0.26	0.123	1.42	61,500 62,500	49,500 50,000	16.5 16.0	69,000 68,500	56,500 56,000	15.0 15.0
2.76	1.01	0.26	0.128	1.25	57,000 56,000	47,000 47,000	12.5 10.5	65,000 64,500	57,500 56,500	6.0 8.5
2.57	0.92	0.24	0.117	2.97	59,500 58,500	47,500 48,000	13.5 10.5	64,000 63,000	53,000 54,500	11.0 9.0

* Lorig and MacLaren.
† Fractured outside gage length.
‡ White fracture.
§ Specimen partially cracked.
‖ Fractured at gage length.

dropped. Precipitation hardening occurred only in samples normalized from 740°C. (1365°F.) or above.* Precipitation hardening itself did not appreciably affect the elongation, but the samples had to be normalized from within a rather narrow range, 10°C. (18°F.), in order to yield precipitation-hardenable material that was not low in ductility owing to solution of temper carbon.

The properties of several malleable irons subjected to a normalizing treatment and then a precipitation treatment are shown in Table 73, from Lorig and MacLaren. It was observed that the average tensile and yield strength were increased, while the elongation was practically unaffected by the solution heat treatment, indicating that no great amount of carbon was redissolved when the copper was brought into solution. The precipitation treatment caused no change in the properties of irons containing 0.6 per cent copper or less. The irons containing 1 per cent copper or more showed an increase in tensile and yield strength of from 2000 to 10,000 lb. per sq. in. with a small but noticeable decrease in elongation.

Smith and Palmer found that, as in the case of copper steels, precipitation hardening could be produced in malleable iron containing copper by cooling from normalizing temperature to the precipitation temperature and holding at the latter temperature for several hours. The properties produced by such a treatment were the same as those produced by first cooling to room temperature and then reheating to the precipitation temperature.

The influence of different heat treatments on the properties of malleable iron containing 2.50 per cent carbon, 1 per cent silicon, and 1 per cent copper was recently studied by Palmer.† The samples used were cast in a commercial foundry and samples of a copper-free iron were tested in order to determine just how copper influenced the properties of the iron. Palmer's conclusions, which were based also on the results obtained in earlier work performed with Smith and on work by Lorig and MacLaren, were:

1. Malleable iron containing about 1 per cent copper will show an increase over the copper-free iron, as malleableized, of about 25 per cent in both

* Later work showed that, in some cases at least, hardening occurred in materials given a solution treatment as low as 700°C. (1290°F.).

† Unpublished report.

tensile strength and yield strength, with about the same percentage loss in elongation.

2. A simple reheating treatment, say 4 hr. at 500°C. (930°F.), will increase the yield strength and tensile strength a further 10 per cent, and again the elongation decreases proportionately.

3. At solution temperatures below the critical, 745°C. (1375°F.), 1 hr. at temperature dissolves sufficient copper to insure, on subsequent reheating, maximum precipitation hardening for the temperature chosen.

4. At solution temperatures above the critical, simply bringing up to temperature is sufficient from a precipitation hardening viewpoint; but since carbon absorption occurs in this range, the actual properties of the irons will depend more on the time and temperature of the solution heat treatment than on subsequent precipitation hardening and may be widely varied.

5. Precipitation hardening to a useful degree, unaccompanied by carbon absorption, occurs only in the relatively narrow solution temperature range of 730 to 745°C. (1345 to 1375°F.).

6. A reheating treatment of 3 to 5 hr. in the range 475 to 525°C. (885 to 975°F.) develops maximum precipitation hardening, accompanied by a maximum decrease in elongation, regardless of the temperature of the solution heat treatment. Longer times tend to improve the elongation, at some sacrifice of tensile strength and yield strength.

7. Precipitation hardening occurs to about the same extent following either normalizing or quenching from the temperature of the solution heat treatment. Normalizing is preferable, for quenching may cause cracks and gives somewhat erratic results.

8. By giving a 1 per cent copper malleable iron a solution heat treatment for 1 hr. at 740°C. (1365°F.), air cooling, and reheating 6 hr. at 500°C. (930°F.), properties of the order given below are possible to obtain, though they have not been consistently obtained with the alloys used in this study.

Tensile strength	70,000 lb. per sq. in.
Yield strength	55,000 lb. per sq. in.
Elongation in 2 in	15 per cent

9. For precipitation-hardening purposes copper in excess of about 0.9 per cent serves no useful purpose in malleable iron and may have a detrimental effect on ductility.

139. Effect of Copper on Tensile Properties of Malleable Cast Iron.—The results in Table 74 indicate that the addition of 1.4 per cent copper increases the tensile and yield strength of experimentally and commercially annealed malleable iron 8,000 to 10,000 lb. per sq. in.

In Table 75 is a summary of results obtained by Lorig and MacLaren on four series of malleable cast irons. Each series contained seven irons with copper content varying from nil to 3 per cent. The bars were annealed at a malleable plant that

TABLE 74.—EFFECT OF COPPER ON TENSILE PROPERTIES OF MALLEABLE IRON*

Heat number	Composition, per cent					
	C	Si	Mn	S	P	Cu
1	2.60	0.92	0.34	0.026	0.174	0.0
2	2.27	0.94	0.32	0.027	0.140	1.39

MECHANICAL PROPERTIES

Annealing furnace	Heat number	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent
Laboratory..		57,200	39,200	11.5
Laboratory..		55,700	39,000	11.0
Laboratory..		64,600	48,900	11.5
Laboratory..		64,500	49,200	10.5
Commercial.		56,200	37,600	10.0
Commercial.		64,500	48,200	13.5

* Lorig and MacLaren (unpublished investigation).

TABLE 75.—EFFECT OF 1 PER CENT OR MORE COPPER ON THE TENSILE PROPERTIES OF MALLEABLE IRON*

Series	Composition, per cent		Tensile strength, lb. per sq. in.			Increase in yield strength, lb. per sq. in.
	Si	C	Average of unalloyed iron	Average of iron with more than 1 per cent copper	Change in strength due to copper	
1	0.80	2.30	64,500	60,000	−4,500	6,000
2	1.00	2.30	60,500	59,500	−1,000	6,000
3	1.20	2.30	50,500	60,000	+9,500	10,000
4	1.00	2.75	44,500	56,500	+12,000	16,000

* Lorig and MacLaren (unpublished investigation).

operates a 6-day annealing cycle. This comprises a period for heating the castings to 815 to 870°C. (1500 to 1600°F.), holding at temperature for 50 hr., then cooling in the oven which is completely sealed against incoming and outgoing air. Tensile

tests indicated that all bars containing more than 1 per cent copper had a yield strength of 40,000 to 50,000 lb. per sq. in. The value increased almost proportionally with the copper content up to 1 per cent. With more copper it remained unchanged to at least 3 per cent copper.

The average increase in yield strength of malleable with 1 per cent or more copper was 6000 to 16,000 lb. per sq. in. and the tensile strength approached 60,000 lb. per sq. in.

Wolf and Meisse,[308] however, found that copper had relatively little strengthening effect on malleable iron as is shown by the following average tensile values:

Copper content, per cent	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent
None	43,100	32,550	8.4
0.25	43,300	33,500	7.6
2.00	47,300	37,800	7.8

As may be seen, the base iron is of a poor quality, and this may account in part for the relatively small influence of copper on the strength. The object of the study was the evaluation of corrosion resistance rather than a study of mechanical properties.

140. Endurance Properties of Copper Malleable Cast Iron.—Two irons of the compositions shown in Table 76 were tested by Lorig and MacLaren.

The copper-free iron 46 was tested only in the annealed state, iron 5 was tested after annealing and also after the annealed specimens had been given a solution treatment for 1 hr. at 735 to 745°C. (1355 to 1375°F.) followed by reheating to 500°C. (930°F.) for 3 hr. to effect precipitation hardening. After the heat treatment the bars were machined into endurance specimens of approximately 0.389-in. diameter and a radius of curvature of 9.875 in. at the reduced section. The tensile and endurance properties of the two irons are summarized in Table 76.

The endurance ratios all fall within the range 0.50 ± 0.05 and the variation cannot be taken to indicate real differences. On the whole, the tensile strength is reflected in the endurance, and no influence on the endurance ratio can be attributed to copper or to precipitation hardening.

TABLE 76.—ENDURANCE PROPERTIES OF COPPER-BEARING MALLEABLE IRON*

Iron number	Composition, per cent					Treatment	Endurance limit, lb. per sq. in. (A)	Tensile strength, lb. per sq. in. (B)	Endurance ratio, $\frac{A}{B}$
	C	Si	Mn	Cu	P				
46	2.43	1.27	0.31	0.042	0.131	Annealed	27,000	50,500	0.54
5	2.48	1.10	0.31	1.24	0.145	Annealed	30,000	60,300	0.50
5	2.48	1.10	0.31	1.24	0.145	Annealed, reheated to 745°C. (1375°F.), reheated to 500°C. (930°F.)	29,500	63,700	0.46

* Lorig and MacLaren.

141. Effect of Copper on the Impact Properties of Malleable Cast Iron.—The influence of copper on the impact resistance of malleable cast iron was investigated by Lorig and MacLaren. Their results, shown in Tables 77, 78, and 79, indicate that copper improves the impact resistance of malleable iron in the "as-malleableized" condition. It is well known that some malleable cast irons become embrittled by heating to temperatures between 315 and 480°C. (600 and 900°F.), the temperatures used in hot-dip galvanizing or sherardizing processes. This embrittlement can be overcome by a heat treatment consisting of heating to and quenching from 550 to 730°C. (1020 to 1345°F.) before galvanizing. Lorig and MacLaren found that the "galvanizing" embrittlement can be considerably reduced or entirely eliminated by adding copper. This will be seen by comparing the drop in impact values on quenching from 450°C. (840°F.); the annealed specimens of any of the series of nearly identical compositions differ only in the copper content.

The results obtained on specimens with varying phosphorus and silicon contents included in the tables illustrate the embrittling effect of these elements. For example, heats 7 and 8 (Table 77) show a comparison of materials of high and low phosphorus content. Heat 7 was not embrittled; heat 8, owing to its high phosphorus content, was brittle in the annealed state and became more embrittled after quenching from 450°C. (840°F.). Normal ductility was restored following quenching from 650°C. (1200°F.) irrespective of subsequent treatments.

TABLE 77.—CHARPY IMPACT VALUES OF MALLEABLE IRON TO SHOW EFFECT OF COPPER ON GALVANIZING EMBRITTLEMENT*

Heat number	Composition, per cent					Average Charpy impact values, ft-lb.							
						Annealed		Heated to 450°C. (840°F.) and quenched		Heated to 650°C. (1200°F.) and quenched		Heated to 650°C. (1200°F.) and quenched; heated to 450°C. (840°F.) and quenched	
	C	Si	Mn	P	Cu	Impact value	Type of fracture†	Impact value	Type of fracture†	Impact value	Type of fracture†	Impact value	Type of fracture†
16	2.18	0.77	0.23	0.129	0.041	3.3	1	3.4	1	3.6	1	3.9	1
3	2.35	0.86	0.30	0.123	1.24	6.6	2	6.2	2	7.4	2	7.6	3
27	2.18	0.80	0.22	0.121	2.03	7.4	2	7.3	2	7.6	2	7.6	2
22	2.36	0.94	0.27	0.132	0.031	3.3	1	2.6	1	2.9	1	3.2	1
41	2.38	1.13	0.28	0.128	1.30	7.2	2	6.2	2	7.2	2	7.4	2
47	2.34	1.04	0.26	0.119	2.68	6.8	2	6.2	2	6.9	2	6.9	2
46	2.43	1.27	0.31	0.141	0.042	4.6	2	1.0	4	5.6	2	5.3	2
42	2.29	1.29	0.26	0.138	1.22	7.1	2	5.3	5	7.5	2	7.1	2
38	2.26	1.24	0.24	0.125	2.97	6.4	2	6.5	2	7.6	2	8.0	2
9	2.78	0.92	0.27	0.127	0.07	4.8	2	3.6	2	4.9	2	4.9	2
11	2.76	1.02	0.28	0.130	1.02	5.4	2	4.5	2	5.5	2	5.5	2
43	2.68	1.01	0.27	0.131	2.91	4.3	2	4.3	2	4.6	2	4.7	2
7	2.38	1.08	0.29	0.027	0.95	3.8	2	3.9	2	3.4	2	4.2	2
8	2.36	1.20	0.29	0.220	0.98	1.4	4	0.5	4	4.8	2	5.0	2
21	2.04	0.67	0.20	0.121	3.04	6.2	2	6.6	2	6.8	2	7.5	2
25	2.13	0.67	0.20	0.10	1.60	4.4	3	4.6	3	5.4	3	5.3	3

* Lorig and MacLaren. † Fracture type: 1—Bright, sparkling. 2—Normal, black. 3—Speckled. 4—White. 5—Slight tendency toward white.

TABLE 78.—CHARPY IMPACT VALUES OF MALLEABLE IRON TO SHOW EFFECT OF COPPER ON GALVANIZING EMBRITTLEMENT*

Heat number	Composition, per cent					Average Charpy impact values, ft-lb.							
						Annealed		Heated to 450°C. (840°F.) and quenched		Heated to 650°C. (1200°F.) and quenched		Heated to 650°C. (1200°F.) and quenched; heated to 450°C. (840°F.) and quenched	
	C	Si	Mn	P	Cu	Impact value	Type of fracture†	Impact value	Type of fracture†	Impact value	Type of fracture†	Impact value	Type of fracture†
46	2.43	1.27	0.31	0.141	0.042	4.8	2	0.8	4	4.9	5	5.3	2
29	2.29	1.19	0.25	0.105	0.60	8.1	2	3.2	4	7.8	5	8.3	2
30	2.31	1.22	0.25	0.110	1.00	8.0	2	7.1	2	7.9	5	8.2	2
42	2.29	1.29	0.26	0.138	1.22	7.2	2	4.8	3	6.9	5	7.1	2
31	2.30	1.29	0.26	0.123	1.42	7.3	2	5.3	5	6.8	5	7.2	2
32	2.34	1.28	0.25	0.122	1.85	7.0	2	5.6	5	7.1	2	7.5	2
38	2.26	1.24	0.24	0.125	2.97	6.9	2	6.2	2	7.1	5	7.3	5
34	2.31	1.08	0.22	0.109	0.63	7.8	2	5.3	3	7.1	5	7.5	5
35	2.27	1.11	0.22	0.106	1.12	8.0	2	7.2	5	7.7	5	7.8	5
45	2.33	1.11	0.27	0.122	2.01	7.5	2	6.8	2	7.9	5	7.9	5
5	2.48	1.10	0.31	0.135	1.24	7.0	2	5.8	5	6.7	5	6.8	2
6	2.45	1.38	0.33	0.122	1.20	5.9	2	2.4	4	6.1	2	6.1	2
36	2.22	1.29	0.25	0.108	1.06	7.3	2	5.6	5	6.8	2	6.3	2
37	2.28	1.25	0.25	0.126	1.63	6.6	2	5.7	5	6.7	5	7.3	5
28	2.17	1.42	0.23	0.123	0.10	8.3	2	1.7	4	8.6	5	8.7	2
33	2.22	1.36	0.24	0.138	3.05	5.8	2	4.4	3	6.7	2	6.4	2

*Lorig and MacLaren. †Type of fracture: 1—Bright, sparkling. 2—Normal, black. 3—Speckled. 4—White. 5—Slight tendency toward white.

TABLE 79.—IMPACT PROPERTIES OF MALLEABLE CAST IRON*

Impact specimen number	Composition, per cent					Charpy impact properties				Percentage change
						As annealed		As annealed, reheated at 450°C. (840°F.) for 30 min., water quenched		
	C	Si	Mn	P	Cu	Impact value, ft-lb.	Type of fracture†	Impact value, ft-lb.	Type of fracture†	
1A	2.36	0.92	0.32	0.206	0	4.4	1	2.2	2	50
3A	2.36	0.92	0.32	0.206	1.23	5.4	1	3.2	2	41
5A	2.36	0.92	0.32	0.206	1.92	5.7	1	5.1	3	10
7A	2.36	0.92	0.32	0.206	2.84	5.8	1	5.4	1	7
9A	2.36	1.17	0.32	0.206	0	5.7	1	2.6	2	54
11A	2.36	1.17	0.32	0.206	1.17	5.2	1	2.7	2	48
13A	2.36	1.17	0.32	0.206	2.01	5.2	1	4.3	3	17
15A	2.36	1.17	0.32	0.206	3.20	5.6	1	4.5	3	20
17A	2.36	1.39	0.32	0.206	0	4.7	1	0.6	4	88
19A	2.36	1.39	0.32	0.206	2.65	4.8	1	2.9	5	40
25A	2.34	0.96	0.30	0.198	0	5.2	3	3.0	2	42
27A	2.34	0.96	0.30	0.198	1.11	6.1	1	3.4	2	44
29A	2.34	0.96	0.30	0.198	1.87	5.8	1	5.3	1	9
32A	2.34	0.96	0.30	0.198	2.10	5.9	1	5.5	1	7
33A	2.34	1.21	0.30	0.198	0	5.5	1	1.7	2	69
35A	2.34	1.21	0.30	0.198	0.92	5.4	1	1.9	5	65
37A	2.34	1.21	0.30	0.198	1.79	5.2	1	4.0	1	23
39A	2.34	1.21	0.30	0.198	2.10	3.9	3	2.0	5	49
41A	2.34	1.36	0.30	0.198	0	5.7	1	1.3	2	77
43A	2.34	1.36	0.30	0.198	1.53	5.0	1	2.6	5	48
46A	2.34	1.36	0.30	0.198	2.51	5.2	1	3.3	3	36
47A	2.34	1.36	0.30	0.198	3.59	5.0	1	3.5	3	30

* Lorig and MacLaren.
† Fracture type:
1—Normal.
2—Bright, sparkling.
3—Mottled appearance.
4—White.
5—Tending toward white.

The embrittling effect of silicon on specimens quenched from 450°C. (840°F.) is illustrated in Table 78. For each series of irons of any given silicon content it will be noted that the copper

practically eliminates the embrittlement when it reaches about 2 to 3 per cent. This is clearly indicated in the last column in Table 79 which gives the relative embrittlement, *i.e.*, the percentage decrease in impact resistance when annealed steels are quenched from 450°C. (840°F.).

Using the data given in Tables 77, 78, and 79, Lorig and MacLaren suggested the following approximate copper requirements for various phosphorus and silicon contents of malleable iron to insure relative freedom from intergranular embrittlement:

Silicon content, per cent	Copper content (per cent) necessary to reduce materially the intergranular embrittlement in malleable cast iron with	
	0.12 per cent phosphorus	0.20 per cent phosphorus
0.90	0.0	1.5
1.10	1.0	
1.20	1.0	2.0
1.30	1.8	3.0+
1.40	3.0	3.0+

142. Influence of Copper on the Corrosion and Acid Resistance of Malleable Cast Iron.—The only investigation on the effect of copper on corrosion of malleable cast iron that has come to the authors' attention is that of Wolf and Meisse.[308] Their tests indicated that copper improves the resistance of malleable iron to the attack by locomotive smoke and decreases the resistance to acid mine water.

For the smoke-corrosion tests bars were cast from four plain malleable irons, and an equal number were cast with the addition of 0.25, 1.0, and 2.0 per cent copper which was added to the ladle. The specimens were suspended in the smoke jacks of a locomotive round-house which were open on the top so that rain could enter. The specimens were removed periodically for inspection, cleaning, and weighing. After 19 months it was apparent that copper materially decreased the corrosion loss. With 1 per cent copper an average decrease in corrosion loss of 25 per cent was noted. Further increase in the copper content did not seem to be warranted because the corrosion rate continued to decrease at a much slower rate.

The corrosion tests in acid mine water were made on malleable irons of the same compositions. The water was made up synthetically to approximate the average composition of mine water found in the Pittsburgh district. The test consisted in alternately immersing the specimens in the water and withdrawing and drying them at 30-min. intervals. The results after five hundred immersions are given below:

Composition, per cent			Loss in weight after 500 immersions, per cent			
C	Mn	Si	No copper	0.25 per cent copper	1 per cent copper	2 per cent copper
2.64	0.29	0.78	5.75	5.35	6.26	5.50
2.90	0.28	0.82	5.71	5.60	5.80	5.37
2.78	0.31	0.80	4.97	5.75	5.63	6.40
2.70	0.26	0.70	4.74	5.30	....	5.80

With test specimens in the form of small castings in the shape of mine hangers, the following average losses for irons of various copper contents after five hundred immersions were obtained:

Copper, per cent	Loss in weight, per cent
0	5.40
0.25	5.75
1	6.30
2	7.15

These results do not prove that there is any advantage in using copper-bearing malleable iron for acid-mine-water service; on the contrary with an increase in copper content the corrosion rate apparently increased.

D. COMPLEX ALLOY CAST IRON

Although nickel-chromium cast irons have been used rather extensively, very little study has been made of the properties of copper-chromium cast iron. This is unfortunate because it is probable that copper could be substituted for part or all of the nickel in the common nickel-chromium iron. On the other hand, too few data are available to determine with certainty whether

or not copper-chromium or nickel-copper-chromium ferritic irons have desirable properties.

Within the past few years austenitic cast irons have come into use and most of these irons contain copper in addition to nickel or some other element that extends the gamma region. Inasmuch as copper is not the predominant alloying element in austenitic irons, work on these irons will not be reviewed in detail in this monograph.

Some data on the influence of tin and zinc in copper irons are available and are reviewed below.

143. Copper-chromium Alloy Cast Irons.—Cast irons with 0.43 to 1.60 per cent copper and 0.50 to 1.25 per cent chromium were studied by Hurst.[320] The specimens were prepared by the centrifugal casting process. The chemical analyses of the series are given in Table 80. Samples 1*c* to 4*c* were prepared by melting refined chromium-alloy pig iron in the cupola and adding pure copper turnings to the molten metal in the ladle. Sample Cu3 was prepared by melting pig iron, ferrochromium, and ferrosilicon in a crucible. Sample Cu1 was made from hematite iron and the ferroalloys.

The results are interpreted by Hurst as follows:

> The sample 1*c*, in spite of the precautions taken, shows an irregular combined carbon content. The remaining samples behaved quite normally and, as will be seen from the Brinell hardness figures, were quite soft and machinable. It is quite clear that this is in part due to the higher copper content, and in this respect the copper behaved like nickel. It may be that somewhat lower copper content of sample 1*c* has a bearing on the higher combined carbon content. Sample Cu1 with a chromium content of 1.25 per cent was quite soft and machinable with Brinell hardness figures ranging from 265 to 300. In spite of the higher silicon content, a great deal of influence must be ascribed to the higher copper content of 1.6 per cent in counteracting the hardening effect of the chromium.

Results of the mechanical tests are summarized in Table 81. Brinell hardness decreased with increasing copper content. In samples 1*c* to 4*c* copper appears to have little effect on the modulus of elasticity and the tensile strength, and in this respect its behavior is the same as in the alloys without chromium. The permanent-set values are slightly increased, as the copper content is increased to 0.94 per cent, and decreased in a sample containing 1.15 per cent copper. The stress-deflection curves

(Fig. 134) show that copper neither introduced any tendency toward brittleness nor increased the toughness.

As may be seen from Table 82, alloys 1*c* to 4*c* hardened when quenched in oil from 820°C. (1510°F.). The tests were not sufficiently comprehensive to allow generalization regarding the influence of copper in quenched gray iron.

Hurst[395] recently pointed out that copper might advantageously replace at least part of the nickel in nickel-chromium iron, for the graphitizing influence of copper is similar to that of nickel and copper is much cheaper than nickel.

A recent note in *Steel*[342] mentioned the use of iron-copper-chromium crankshafts in a well-known automobile, but more

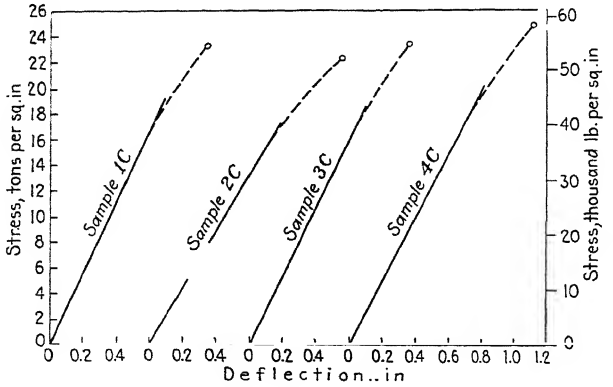


FIG. 134.—Stress-deflection curves of copper-chromium cast iron. (*Hurst.*[320])

recent information indicates that the alloy is a steel rather than a cast iron.

A trade-named material, stated to be an effective substitute for nickel in cast iron, is on the American market and consists essentially of a nickel-copper alloy.

144. Austenitic Irons.—The properties of austenitic alloys containing nickel, copper, and chromium were described by Ballay,[224,276] Vanick and Merica,[273] Hurst,[320] and Guillet and Ballay.[319] Austenitic nickel-chromium irons with a high silicon content were described by Norbury and Morgan.[330] It was stated that the corrosion-resistance of this iron was improved by the addition of copper.

The austenitic irons are non-magnetic, are resistant to attack by many electrolytes, and resist growth when heated to elevated

temperatures. They are soft and readily machinable if they do not contain too much chromium.

TABLE 80.—COMPOSITION OF COPPER-CHROMIUM CAST IRONS*

Sample number	Composition, per cent							
	Total C	Combined C	Graphite	Si	Mn	P	Cu	Cr
1*c*	3.22	1.55	1.67	2.10	0.62	Under 0.10	0.56	0.43	0.57
2*c*	3.31	0.63	2.68	2.05	0.70	Under 0.10	0.59	0.64	0.60
3*c*	3.30	0.68	2.62	2.07	0.66	Under 0.10	0.58	0.94	0.50
4*c*	3.24	0.58	2.66	2.02	0.70	Under 0.10	0.	1.15	0.56
Cu 3	3.43	0.78	2.65	2.58	0.43	Under 0.10	0.51	0.51	0.48
Cu 1	3.68	0.88	2.80	2.85	Not determined	Under 0.10	0.047	1.60	1.25

* Hurst.[320]

TABLE 81.—MECHANICAL PROPERTIES OF COPPER-CHROMIUM ALLOY CAST IRONS*

Sample number	Modulus of elasticity $\times 10^{-6}$, lb. per sq. in.	Tensile strength, lb. per sq. in.	Modulus of rupture, lb. per sq. in.	Permanent set, per cent	Area of stress-deflection curve	Proportional limit, lb. per sq. in.	Brinell hardness
1*c*	17.9	51,700	82,600	7.3	27.5	31,400	360
2*c*	17.5	51,000	81,700	9.4	31.5	31,400	297
3*c*	17.5	49,700	79,500	9.6	27.5	35,900	264
4*c*	17.0	50,800	81,300	8.1	34.5	35,900	268
Cu 3	15.4	.....	80,800	13.0	44 to 52	22,400 to 26,900	
Cu 1	....	.....	.....	....	.....	.....	285

* Hurst.[321]

TABLE 82.—EFFECT OF HEAT TREATMENT ON HARDNESS OF COPPER-CHROMIUM CAST IRONS*

Sample number	Brinell hardness				
	As cast	Oil quenched from 820°C. (1510°F.)	Tempered at 330°C. (625°F.)	Tempered at 500°C. (930°F.)	Air hardened from 820°C. (1510°F.)
1c	360	520	450	315	315
2c	297	540	450	315	315
3c	264	560	368	315	315
4c	268	520	357	285	315

* Hurst.[320]

The irons discussed by Vanick and Merica have compositions within the following limits:

Element	Percentage	
	Minimum	Maximum
Total carbon	2.75	3.10
Silicon.....	1.25	2.00
Sulphur.....	0.04	0.120
Phosphorus.	0.04	0.30
Manganese..	1.00	1.50
Nickel.....	12.00	15.00
Copper.....	5.00	7.00
Chromium..	1.50	4.00

The mechanical properties of such irons lie within the following ranges:

Transverse strength, arbitration bar*..... 2,500 to 4,000 lb.
Transverse deflection, arbitration bar*..... 0.2 to 0.3 in.
Tensile strength of 1.25-in. section..... 20,000 to 35,000 lb. per sq. in.
Brinell hardness..... 120 to 170

* The bar used was 1.25 in. in diameter, broken on a 12-in. span.

The strength and hardness increase as the silicon content increases while the deflection decreases.

The machinability of iron containing 14 per cent nickel, 6 per cent copper, and 2 per cent chromium is the same as that of ordinary gray iron. Increasing the chromium content to 3 per

cent practically halves the machinability as measured by cutting speed giving a certain tool life. The coefficient of linear expansion of the iron for temperatures up to 600°C. (1110°F.) is about 50 per cent greater than that of ordinary gray iron.

The resistance to growth and oxidation of the austenitic iron at 815°C. (1500°F.) is illustrated in Fig. 135.

The copper in the iron serves the purpose of decreasing the amount of nickel required to give an iron of the desired proper-

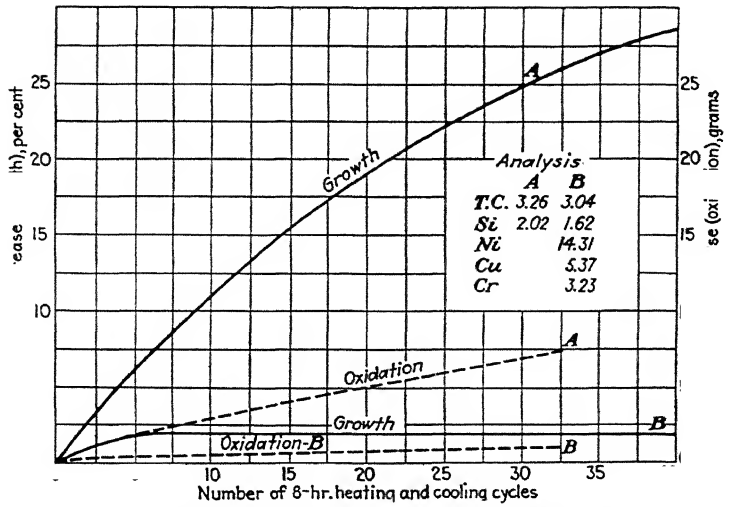


FIG. 135.—Oxidation and growth of ordinary iron and an austenitic iron at 815°C. (1500°F.). (*Vanick and Merica.*[273])

ties, some 6 per cent copper replacing the same amount of nickel. The copper does not seem to affect the corrosion rate in many corrosives; it definitely improves the resistance to some reagents, such as sulphuric acid.

145. Tin and Zinc in Copper Cast Irons.—Skorčelletti and Šultin[304] found that tin considerably improves the resistance of gray cast iron to acid attack. Encouraging results were also obtained by adding tin to copper cast iron. The best results were obtained with the ratio of tin to copper at 1 to 8. From 1.3 to 1.5 per cent of the intermediate alloy (Sn-Cu) was found to be sufficient for best results. Further increase did not appear to have any advantage in improving the acid-resisting properties, with the exception of resistance to nitric acid where the increase

of the total tin and copper content up to 3.5 per cent was found to be advantageous.

The mechanical properties of cast iron seem to be affected unfavorably by the addition of tin. However, the properties even with 3.5 per cent combined copper and tin content are still sufficiently high so that the cast iron is claimed to be applicable for use in chemical apparatus not requiring especially high strength.

The compositions and the results of tests are given in Table 83. The alloys were made in a Kryptol furnace, and 2.5-kg. (5.5-lb.) melts cast in dry sand. A decrease in the graphite content was observed when tin was added to the irons.

The acid resistance of the irons was determined by the loss of weight of small cylindrical specimens immersed in aerated acids at room temperature.

Spencer and Walding[335] showed that, when brass was added to cast iron, most of the zinc was volatilized. For example, when 1 per cent and 0.25 per cent brass were added to cast iron, the remaining quantities of zinc were 0.04 and 0.02 per cent respectively. They also noted that more zinc from brass additions remained in the austenitic nickel-copper-chromium iron than in plain cast iron. This is thought to be due to the presence of the large amounts of nickel and copper; these metals tend to alloy with the zinc.

E. AUTHORS' SUMMARY

1. Alloying copper with cast iron does not present any difficulties. Casting properties are little affected by copper, although the fluidity appears to be somewhat improved.

2. Copper apparently accelerates graphitization of cast iron during solidification, although the evidence is not quite convincing, and the effect may be entirely obscured by the differences in the iron brought about by variations in the manufacturing process.

3. The structure of the matrix of gray cast iron is little affected by copper. Since the carbon-eutectoid composition is not displaced by copper, pearlitic structures are obtained with the same carbon concentration as in copper-free cast irons.

4. The strength and hardness of cast iron are increased as the copper content increases up to 1 per cent; beyond this concen-

TABLE 83.—EFFECT OF COPPER AND TIN ON MECHANICAL AND ACID-RESISTING PROPERTIES OF GRAY CAST IRON*
Total carbon 3.5 per cent, silicon 1.5 per cent, manganese 0.5 per cent, phosphorus and sulphur under 0.05 per cent each

Composition, per cent				Modulus of rupture, lb. per sq. in.	Tensile strength, lb. per sq. in.	Hardness		Loss in weight, g. per hr.†							
								Nitric acid		Sulphuric acid		Hydrochloric acid		Acetic acid	
Graphite	Sn	Cu	Cu + Sn			Brinell	Rockwell	10 per cent	20 per cent	10 per cent	20 per cent	10 per cent	20 per cent	10 per cent	20 per cent
2.86	....	....	....	71,100	36,710	227	17	1,406	1,682	144	134	121	169	10.6	9.6
2.82	....	....	....	71,300	32,730	204	16.2	1,224	1,044	206	117	155	172	9.6	10.9
2.13	0.54	....	....	67,300	35,860	272	30.6	761	777	34	60	64	128	3.2	3.2
2.02	2.0	....	....	55,600	27,860	302	35.5	580	655	27	49	60	157	3.6	3.2
2.65	....	0.40	....	73,700	39,420	223	20.3	1,292	1,630	155	177	57	66	4.8	4.5
2.50	....	1.66	....	88,300	49,800	274	30	948	891	192	148	23	38	20	12.4
2.32	0.82	0.50	1.32	65,300	32,160	316	33.6	1,198	842	10	18	23	44	2	2.3
2.17	0.80	0.51	1.31	64,700	28,460	324	34.3	1,005	812	8	21	23	49	2.2	2.2
2.12	2.88	0.65	3.53	36,000	.....	352	37.9	363	275	12	28	15	54	3.2	2.4

* Skorčelletti and Šultin.[304]

† Total on cylindrical specimens, 12 mm. (0.476 in.) in diameter, 12 mm. (0.476 in.) high.

tration the strength and hardness continue to increase but at a very slow rate.

5. Precipitation treatment apparently does not produce any effect on pearlitic gray cast iron. This requires further study in relation to ferritic irons.

6. The resistance of cast iron to acid attack and to atmospheric corrosion is apparently increased by copper, the maximum effect being observed with 0.2 to 0.5 per cent copper.

7. Further study should be made of copper-chromium irons.

8. Hurst's suggestion that copper can be effectively substituted for some of the more expensive nickel in nickel-alloyed cast iron deserves attention and further experiment.

9. In malleable iron copper accelerates the graphitization of cementite, thereby introducing the possibility of reducing the time of heating for malleableization. It increases the tensile and yield strength and slightly decreases the ductility.

10. The endurance limit of malleable cast iron is increased by copper, in about the same ratio as the tensile strength. The impact resistance of malleable iron in the annealed state is improved by copper.

11. Copper considerably reduces the susceptibility of malleable cast iron to galvanizing embrittlement.

12. Further improvement in the mechanical properties of malleable iron containing copper may be accomplished by a precipitation-hardening treatment.

13. Limited experiments indicated that copper improves the resistance of malleable cast iron to corrosion in smoke-laden atmosphere.

14. Austenitic nickel-chromium cast irons containing from 5 to 7 per cent copper possess superior corrosion-, acid-, and heat-resisting properties.

CHAPTER XI

COPPER IN COMPLEX STEELS AND OTHER ALLOYS

Complex Alloys Including Carbon-free Materials—Copper in Complex Low-alloy Steels—Copper in Corrosion-resistant Alloys and in Tool Steels—Authors' Summary

Ternary and more complex alloys of iron and copper are discussed below. Although none of the ternary or quaternary carbon-free alloys of iron and copper has been used commercially, some attention has been paid to their constitution and properties. Low-alloy steels containing copper have been used commercially, and considerable information on the properties of certain of these steels is available. A few investigations have been concerned with the influence of small amounts of copper in corrosion-resistant alloys and in tool steels.

A. COMPLEX COPPER ALLOYS INCLUDING CARBON-FREE MATERIALS

Results of studies of ternary equilibria in the system iron-copper-nickel have been reported by several investigators, an approximate equilibrium diagram for the iron-copper-manganese system has been worked out, and the iron-copper-nickel-manganese system has been investigated. A considerable number of data on the properties of the iron-copper-nickel system are available, but there is very little information in the literature on the properties of other complex carbon-free copper alloys.

146. The Iron-copper-nickel Diagram.—Vogel,[61] in 1910, outlined the general features of the portions of the diagram involving a liquid phase and reported the results of thermal and microscopic studies from which he was able to construct a diagram. His outline of the high-temperature portion of the system is undoubtedly correct except for modifications near the iron corner necessary to account for the existence of delta iron. In 1929, Chevenard and coworkers[230] attempted to determine parts of two room-temperature boundaries by dilatometric methods. At the World Engineering Congress in 1929,

Tasaki[250] reported the results of a study of iron-copper-nickel alloys and presented a complete diagram for the system.

Before discussing the available data on the iron-copper-nickel system it may be well to outline the diagram. Copper and nickel form a continuous series of solid solutions at all temperatures. At temperatures at which gamma iron is stable, iron and nickel form a continuous series of solid solutions. As was brought

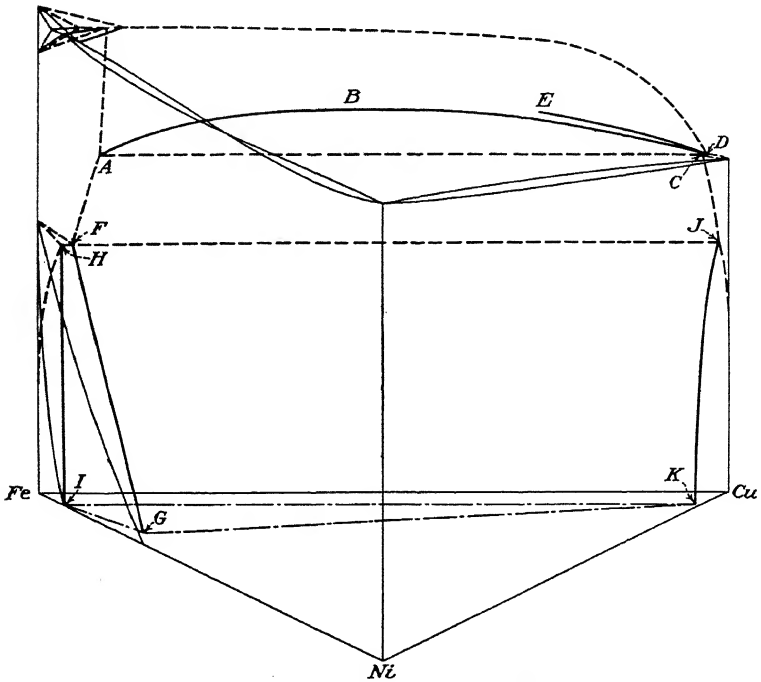


FIG. 136.—The iron-copper-nickel diagram.

out in Chapter II, iron and copper do not form a continuous series of solid solutions and a peritectic reaction occurs in which a copper-rich melt reacts with an iron-rich solid to form a copper-rich solid. Neither copper nor nickel tends to raise the temperature at which alpha iron is stable, and as the solidification range of any ternary alloy is above the temperature of the alpha-gamma transformation in pure iron it is apparent that except for the regions in which delta iron is stable the system (for the portion involving a liquid phase) may be described as one in which two

pairs of the components are completely soluble in the solid and one pair has a miscibility gap in the solid. The system differs from the one adequately described by Tammann[151] and Masing[365] in that a peritectic instead of a eutectic reaction occurs in the binary system containing the miscibility gap.

The general features of the iron-copper-nickel system may be visualized by reference to Fig. 136, which shows the location in space of the lines along which one phase is in equilibrium with two other phases, and Fig. 137, which shows the projection of

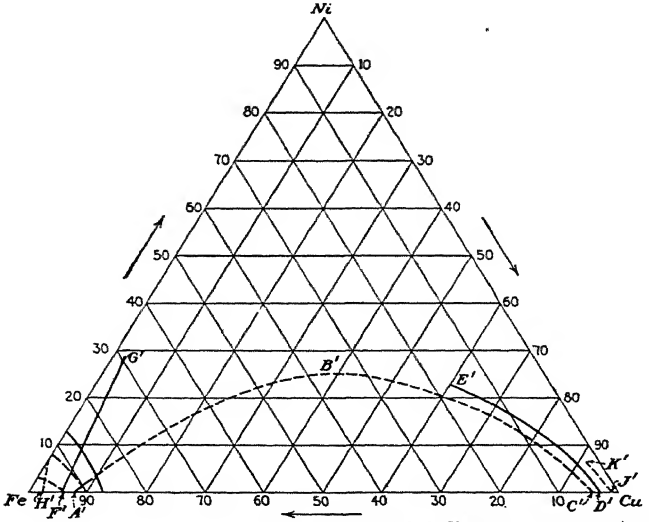


FIG. 137.—Projection of lines in iron-copper-nickel diagram on concentration plane.

these lines on the composition triangle. In the iron corner, delta iron is formed on cooling; since peritectics occur in the iron-copper as well as in the iron-nickel system, the peritectic must remain in the iron-copper-nickel system, but with one degree of freedom. This portion of the diagram is similar to the high-temperature portion of the iron corner of the iron-copper-carbon diagram and does not need further description here.

Alloys whose compositions lie outside the area $A'B'E'D'$ form a single phase on solidification, and except for those that first precipitate delta iron on solidification they solidify as do alloys in a ternary system whose components are miscible in all propor-

tions in the solid. Since iron-nickel liquidus-solidus has a minimum, surfaces of the iron-nickel-copper system must touch over a portion of their extent.

Alloys in field $A'B'C'$ first form an iron-rich phase on cooling. On continued cooling the composition and temperature of this solid phase reach a point on line AB and, at the same instant, the melt reaches a point on line DE. The melt then reacts with the iron-rich solid to form a copper-rich solid whose composition is along line BC. On further extraction of heat, solidification proceeds by a univariant reaction between the iron-rich solid whose composition varies along line BA, a copper-rich solid whose composition varies along line BC, and the melt whose composition varies along line ED. Solidification is completed by exhaustion of the melt during this reaction, resulting in a two-phase alloy, the compositions of the phases being given by the intersection of tie-lines with curve ABC, the tie-line passing through the perpendicular representing the total composition of the alloy and being, in this system, approximately parallel to the Fe-Cu side of the diagram. The ruled surface formed by isothermal straight lines almost parallel to AC and connecting AB with CB forms the solidus for alloys in field $A'B'C'$. Point B is at a higher temperature than AC. It would be desirable to indicate tie-lines in the illustrations, but data enabling their location are not available. As the Fe-Cu side is approached they tend to become parallel to AC; point B is the point where the direction of the tie-lines becomes tangent to curve ABC. We can only hope that B as shown is somewhere near its true position. If we designate the phase whose composition and temperature is fixed by line AB as γFe and the phase whose composition and temperature are fixed by the line BC as γCu, point B gives the composition and temperature at which γFe and γCu become identical; *i.e.*, B is the critical point.

It may be well to mention that Tasaki showed line DE as intersecting ABC at B; points B and E became identical. It does not appear to the authors that it is necessary for points B and E to be identical, and in the absence of experimental data indicating Tasaki's construction to be correct it is believed that Vogel's construction, shown in the diagrams given here, should be considered as the more probable.

None of the investigators of the ternary iron-copper-nickel system has taken cognizance of the field of liquid immiscibility

in the iron-copper system. Nickel must increase the temperature at which iron-copper alloys yield two immiscible layers and the field of liquid immiscibility in the ternary system must be a bulge extending inward from the iron-copper side but not touching the liquidus.

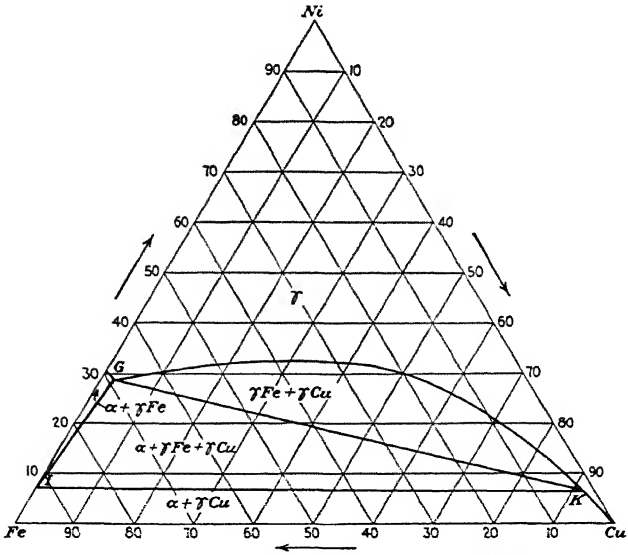


FIG. 138.—Isothermal section of iron-copper-nickel diagram at ordinary temperature as constructed from diagrams given by *Tasaki*.[250]

A eutectoid transformation is observed in iron-copper alloys. With the addition of nickel the temperature of this transformation is lowered and it does not take place at a constant temperature. In other words, the invariant eutectoid transformation in the iron-copper system becomes a univariant eutectoid reaction in the ternary system. During this reaction gamma iron along line *FG*, alpha iron along line *HI*, and gamma-copper-rich phase along line *JK* are in equilibrium. The reaction is:

$$\rightarrow \alpha\text{Fe} + \gamma\text{Cu}$$

The three-phase field at room temperature is shown by the triangle *IGK* in Fig. 136.

The isothermal section of the diagram for ordinary temperature is shown in Fig. 138, constructed from Tasaki's diagram. This section is drawn as though iron and copper were completely

immiscible at ordinary temperature, a condition that is almost realized. In the three-phase field alpha is the iron-rich phase represented by point *I*, gamma iron is the phase represented by point *G*, and gamma copper the ternary phase represented by point *K*. At a temperature just above that at which alpha iron is stable, say 910°C., an isothermal section consists of two fields, one a two-phase field in which gamma iron and gamma copper are in equilibrium and the other a single-phase field. The two-phase field is bounded approximately by the line *A'B'C'* of Fig. 137. According to Tasaki, the extent of this field is slightly increased on falling temperature, which is to be expected.

147. Experimental Data on the Iron-copper-nickel Diagram.—Alloys used by Vogel[61] were prepared from electrolytic copper, electrolytic nickel, and a Krupp iron containing 0.07 per cent carbon, 0.02 per cent silicon, 0.09 per cent manganese, 0.07 per cent phosphorus, 0.03 per cent sulphur, and 0.02 per cent copper. Charges of from 20 to 30 g. were melted in porcelain crucibles in an atmosphere of nitrogen, heated to about 100°C. above the liquidus, and cooling curves taken to 1000°C.; the cooling velocity was not stated. In order to prevent undercooling the melts were stirred until crystallization began. Specimens for microscopic examination were annealed at a temperature of 100°C. below the solidus in order to promote homogenization. Tasaki[250] prepared his alloys from electrolytic iron, electrolytic copper, and nickel containing 0.14 per cent carbon, 0.20 per cent iron, and 0.01 per cent sulphur. They were melted in a Tammann furnace in an unglazed porcelain crucible. Cooling curves were obtained, the alloys examined microscopically after quenching from various temperatures, and electric-resistance-temperature curves obtained for some of the iron-rich alloys. Tasaki's work was but briefly described and little explanation of the diagrams presented was given.

The isothermal lines of Fig. 139 are those drawn by Vogel, the solid lines indicating liquidus isothermals and the dotted lines solidus isothermals. The liquidus temperatures obtained by Tasaki are also shown on the diagram. They are in fair agreement with Vogel's curves but are not sufficiently numerous to allow construction of isothermal lines.

The solid lines in Fig. 140 are the boundary for the single-phase field at room temperature as given by the several investigators. Line 1 was given by Vogel,[61] line 2 by Chevenard and associates,[230] and line 3 by Tasaki.[250] Line 4 was given by Roll[373]

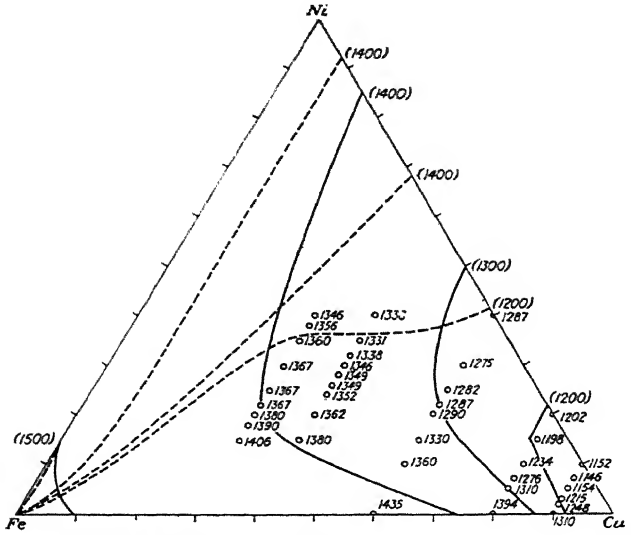


FIG. 139.—Isothermal lines for liquidus (solid lines) and solidus (dotted lines) as drawn by *Vogel*.[61] Liquidus temperature determined by *Tasaki*.[250]

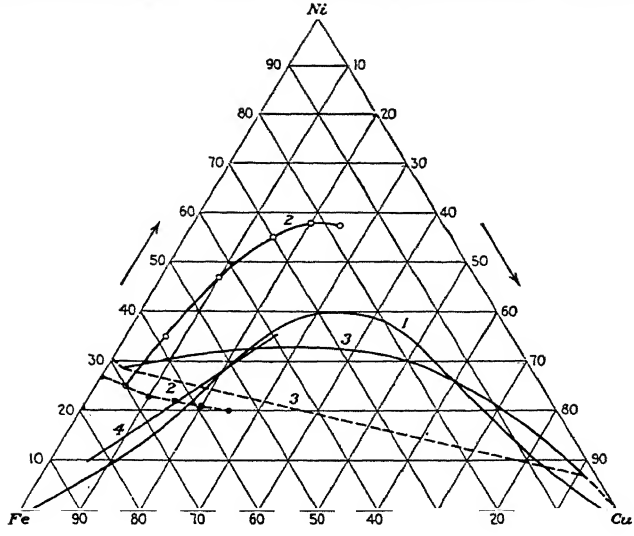


FIG. 140.—Boundary of single-phase field (solid lines) and limit of existence of alpha iron as determined by several investigators. Lines are supposedly for ordinary-temperature equilibrium. Lines 1 by *Vogel*,[61] 2 by *Chevenard and associates*,[230] 3 by *Tasaki*,[250] and 4 for alloys containing 1.5 per cent carbon as reported by *Roll*.[373]

to show the boundary for alloys containing 1.5 per cent carbon as determined by microscopic examination. On account of the nearness of this line to Vogel's line, Roll concluded that carbon did not shift the position of the line and that his work confirmed Vogel's location of the solubility limit. Line 2 was obtained from dilatometric curves obtained with alloys containing small quantities, from 0.28 to 0.80 per cent, of manganese. The curve shown as line 2 is in such poor agreement with the lines determined by other workers that it must be considered improbable. The dilatometric method is certainly an indirect procedure for determining the solubility limit in this instance. Chevenard assumed that certain anomalies in the curves indicated the solution of one phase in another and that if these were observed the alloy consisted of two phases at room temperature. It seems possible to the authors that the anomalies in question were due to some other phenomenon and that they did not even approximately indicate the solubility limit in question.

The determination by Kussmann and Scharnow[237] of the coercive force of a series of annealed iron-nickel-copper alloys containing equal amounts of iron and nickel indicated that the solubility line in the section between 50 per cent iron, 50 per cent nickel, and the copper corner was between 15 and 19 per cent copper. This would place it between curves 1 and 2.

The dotted curves in Fig. 140 indicate the limit of stability of alpha iron at ordinary temperature. Line 3 was taken from Tasaki's diagrams and line 2 was obtained by Chevenard and associates from dilatometric curves. In the ternary system the line, or rather lines, must be as shown by line 3, and not curved as drawn by Chevenard and associates.

Vogel was not able to locate line *DE*, in Fig. 137, precisely. Tasaki drew it very close to line *BC*, and in fact intersecting *ABC* at *B*, but his reasons for locating it as he did are not evident.

The section of the ternary diagram at 60 per cent copper as drawn by Tasaki is shown in Fig. 141. As this diagram shows, the surface separating the single-phase space from the two-phase space recedes from the iron-copper side as temperature is decreased. The loop *ABC* of Fig. 136 is therefore enlarged as temperature decreases. Below about 1000°C. the dimensions of the loop remain almost unchanged, and from ordinary temperature to about 1000°C. the immiscibility region approaches a section of a vertical cylinder.

The only study of transformations in solid iron-rich alloys is that by Tasaki, who obtained electric-resistance-versus-temperature curves and made microscopic examination of the quenched alloys. His work indicates that the reactions took place as described above. Inasmuch as the exact method of obtaining

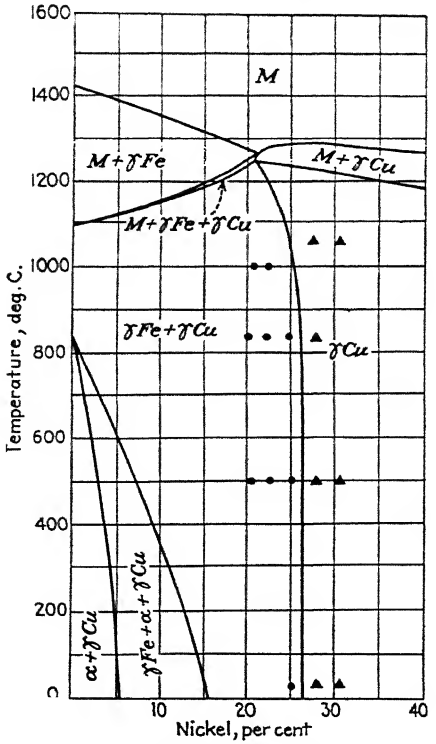


FIG. 141.—Section of the iron-copper-nickel diagram at 60 per cent copper as drawn by

these curves was not described and none of the curves was shown, it is impossible to estimate the reliability of the critical temperatures reported. It appears highly probable, however, that the reactions occur as outlined and that the equilibrium lines in question are approximately located by lines *HI*, *FG*, and *JK* in Fig. 136.

The authors think that Tasaki's diagram modified as mentioned above permits the construction of the most probable

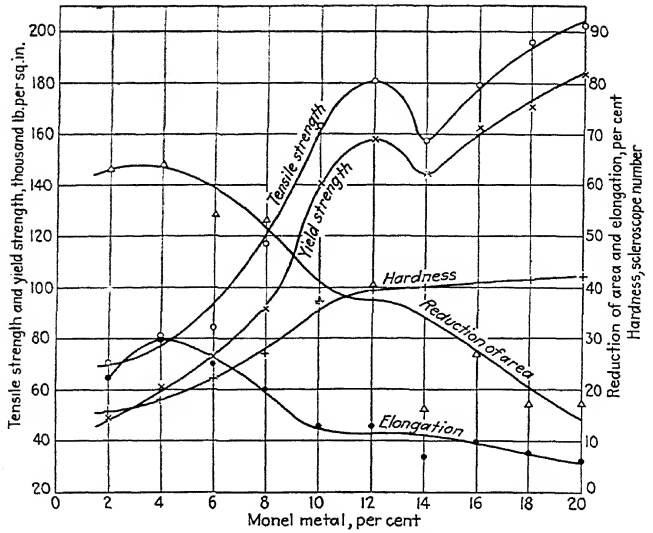


FIG. 142.—Properties of forged alloys of Monel metal (two-thirds nickel and one-third copper) and electrolytic iron. (*Burgess and Aston*[57] and *Roush.*[59])

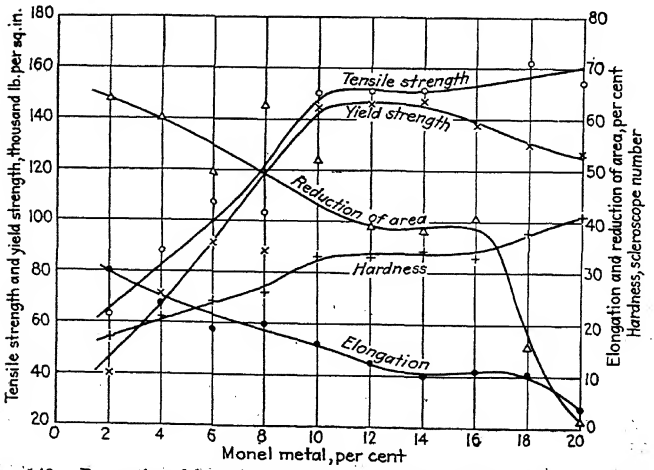


FIG. 143.—Properties of forged and annealed alloys of Monel metal and electrolytic iron. (*Burgess and Aston*[57] and *Roush.*[59])

diagram, but that almost none of the surfaces or lines in the diagram can be located with certainty.

148. Properties of Iron-copper-nickel Alloys.—A series of alloys was prepared by Burgess and Aston[57] by melting electrolytic iron with various percentages of Monel metal. As Monel metal contains approximately 67 per cent nickel and 33 per cent copper, the resulting alloys were located on a line in the composition triangle extending from the iron corner to a point

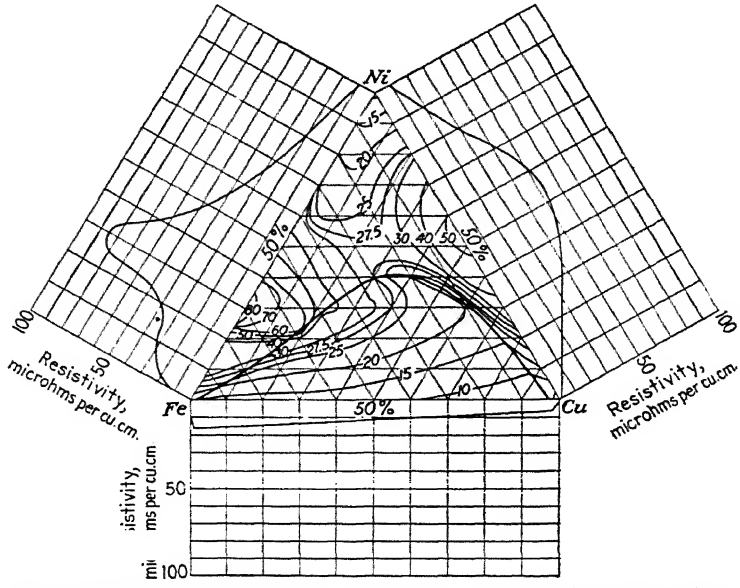


FIG. 144.—Curves of equal electric resistivity of annealed iron-copper-nickel alloys. (*Kosti*

on the nickel-copper side representing the composition of Monel metal. In addition to copper and nickel the Monel metal contained either 1.62 or 2.18 per cent manganese. Each melt weighed approximately 1 lb. and all alloys were hot forged into bars 0.4 in. in diameter. The properties of the forged alloys are shown in Fig. 142 and those of the annealed alloys in Fig. 143. The figures contain scleroscope-hardness values reported by

Some of the physical properties of a group of iron-copper-nickel alloys were determined by Kosting.[207] About thirty alloys whose compositions spread over the entire diagram were used.

Some of the alloys were made by melting electrolytic iron, electrolytic copper, and electrolytic nickel together with about 0.4 per cent manganese in a vacuum. Armco iron was used in preparing other alloys, which were melted under a glass slag and to which 0.1 per cent aluminum, 0.5 per cent manganese, and 0.15 per cent magnesium were added before casting. Electric properties were obtained from the alloys in the form of annealed wire and expansivity was obtained from annealed cast rod. The

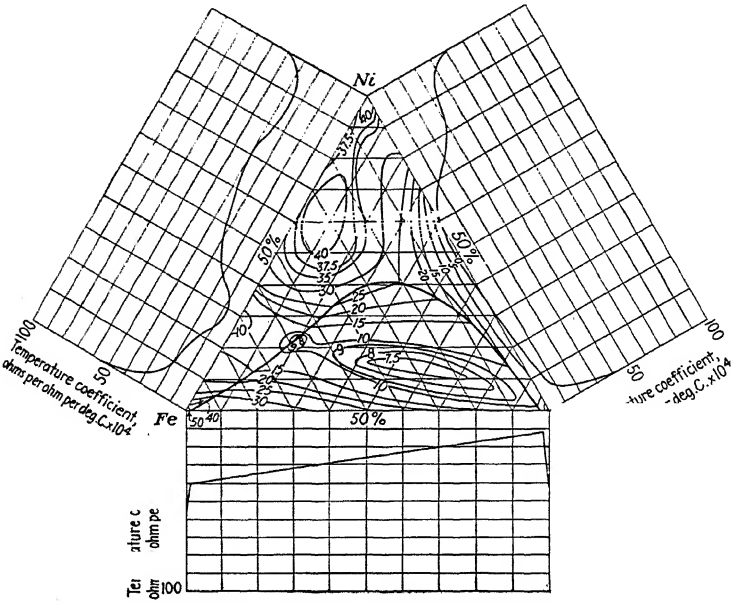


FIG. 145.—Curves of equal temperature coefficient of electric resistance of annealed iron-copper-nickel alloys.

annealing temperatures ranged from 800 to 950°C. (1470 to 1740°F.). Curves of equal resistance of the ternary alloys are shown in Fig. 144. This figure shows the line separating the single-phase region from the polyphase region as given by Vogel, and the lines of equal resistance are drawn to take account of the change of nature of the alloys near the curve. However, the alloys investigated were not sufficiently numerous to permit a determination of the solubility line from their physical properties. The figure shows that the addition of copper to iron-nickel alloys and the addition of iron to copper-nickel alloys lowers the

resistance. Figure 145 shows curves of equal temperature coefficients of electric resistance for the range 20 to 100°C. Kosting stated that the most interesting region was that bounded by 2 to 15 per cent copper and 50 to 75 per cent nickel, where the temperature coefficient is above 0.004 per degree. The addition of iron to the copper-nickel alloys of low temperature coefficient of resistance (Constantan) increased the coefficient. The

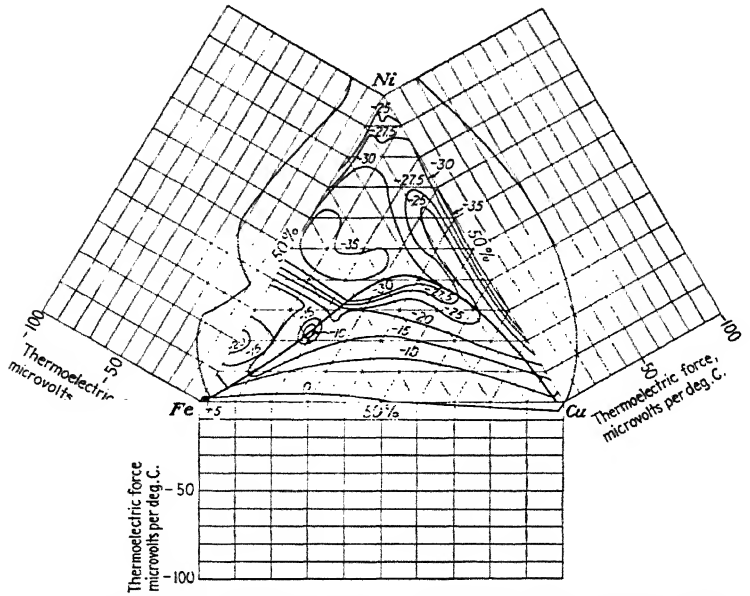


FIG. 146.—Curves of equal thermoelectric force versus copper in the range 20 to 100°C. (70 to 210°F.) of annealed iron-copper-nickel alloys. (*Kosting.*[207])

thermoelectric force of the alloys versus copper for the range 20 to 100°C. may be seen by reference to Fig. 146. Thermoelectric data for higher temperatures were also obtained. Thermal expansion curves for several of the alloys near the composition of Invar are shown in Fig. 147. Addition of copper to Invar increased the expansivity at low temperatures and raised the temperature at which rapid expansion occurred. The alloys whose expansion is shown in Fig. 147 had the compositions shown at the top of page 324.

In so far as is known, carbon-free iron-copper-nickel alloys containing appreciable amounts of copper have not been used

Number	Composition, per cent		
	Ni	Fe	Cu
F 6	36	64	0
F 7	33.3	59.5	7
F 8	30.5	54.5	15
F 10	....	....	38
F 11	18.5	33.5	48
F 12	12.5	22.5	65

commercially, although it was claimed[55] that the alloy containing approximately 65 per cent iron, 25 per cent nickel, and

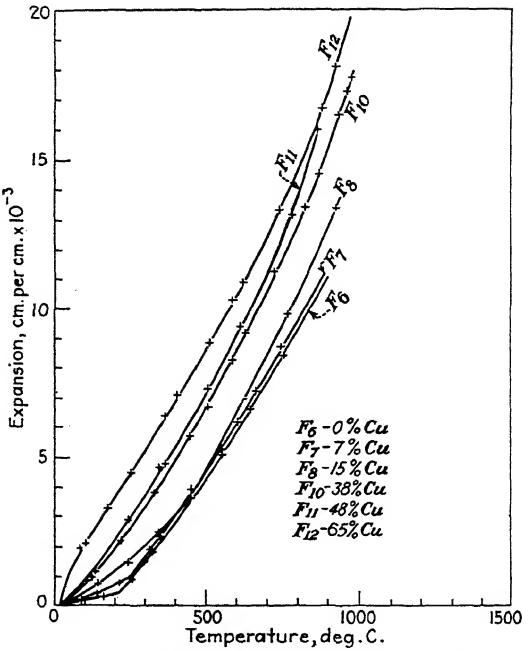


FIG. 147.—Thermal expansion of Invar and melts of Invar and copper. (*Kosting.*[207])

10 per cent copper had desirable mechanical properties and was "non-corrosive." Alloys of the Permalloy type mentioned by

Campbell[153] may contain several per cent of copper, the function of the copper being to modify the electric and/or the magnetic properties of the iron-nickel alloys containing between 70 and 80 per cent nickel. These alloys are also discussed in an anonymous article.[274] Stout[336] recently wrote that he had produced iron-copper-nickel alloys by simultaneous deposition of the components.

149. The Iron-copper-manganese Diagram.—In attempting to determine the iron-copper-manganese diagram Parravano[67] obtained cooling curves for 49 alloys and made a microscopic examination of the normally cooled and annealed alloys. The iron used in preparing the alloys contained 0.050 per cent carbon, 0.067 per cent manganese, 0.010 per cent silicon, 0.003 per cent sulphur, and 0.042 per cent phosphorus. The manganese contained 0.99 per cent iron, 0.57 per cent silicon, and 0.53 per cent aluminum. The copper was stated to be 99.92 per cent pure. The alloys were melted in a carbon-tube furnace in a magnesia crucible. The annealed specimens were held at temperatures between 780 and 900°C. (1435 and 1650°F.) for different periods of time, depending on the ease of removing the cored structure.

The iron-copper-manganese diagram was found to be much like the iron-copper-nickel diagram, the most striking difference being that the univariant reaction between a liquid copper-rich phase, a solid iron-rich phase, and a solid copper-rich phase occurred at lower temperatures as the manganese content increased, or the line corresponding to *DE* and the surface *ABC* in Fig. 136 sloped downward in the iron-copper-manganese system instead of upward as shown in the figure. Parravano's interpretation of his data was based on the assumption that both iron and copper formed a continuous series of solid solutions with manganese, therefore, no account was taken of the existence of delta iron or allotropic modifications of manganese. His data are not adequate for the construction of a diagram showing those unconsidered modifications.

Figure 148 shows liquidus temperatures determined by Parravano and isothermal lines for the liquidus surface. The heavy dashed line near the copper corner shows the approximate position of the univariant line along which a liquid phase is in equilibrium with two solid phases. The exact position of this line could not be determined. Figure 149 shows the solidus temperatures and isothermal lines for the solidus. It also shows the miscibility

gap (heavy dashed line) determined by microscopic examination of annealed specimens. This probably represents the miscibility gap at some temperature between the solidus and ordinary temperature. Equilibria in the solid alloys have received no attention.

150. Iron-copper-nickel-manganese Alloys.—In studying these alloys Parravano[68] obtained cooling curves for 84 alloys

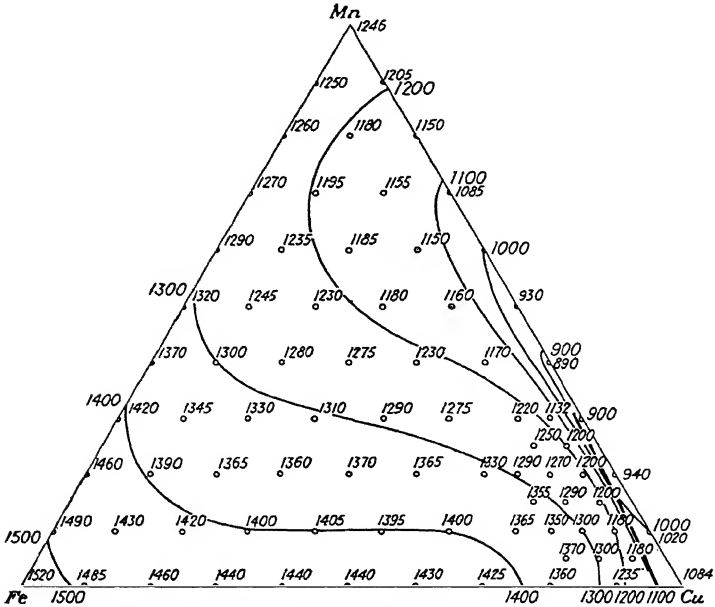


FIG. 148.—Liquidus temperatures and isothermal lines in the iron-copper-manganese system. (*Parravano.*[67])

in the quaternary system. The compositions of the iron, manganese, and copper used in preparing the alloys were given in discussing the iron-copper-manganese system above. The nickel used had a purity of 99.2 per cent.

In order to work out a quaternary system it is necessary to know the six binary diagrams for pairs of the constituents and the four ternary diagrams for the possible combinations of three of the constituents. Since little is known about some of the binary systems and most of the ternary systems, it is obviously impossible to construct a complete quaternary diagram. All that Parravano attempted to do was to determine the tem-

peratures at which the alloys begin to solidify and at which solidification is completed.

The compositions of quaternary alloys can be represented by a tetrahedron. In such a representation the corners designate the four components, the six edges the binary alloys, and the four faces the ternary alloys. Points within the tetrahedron represent

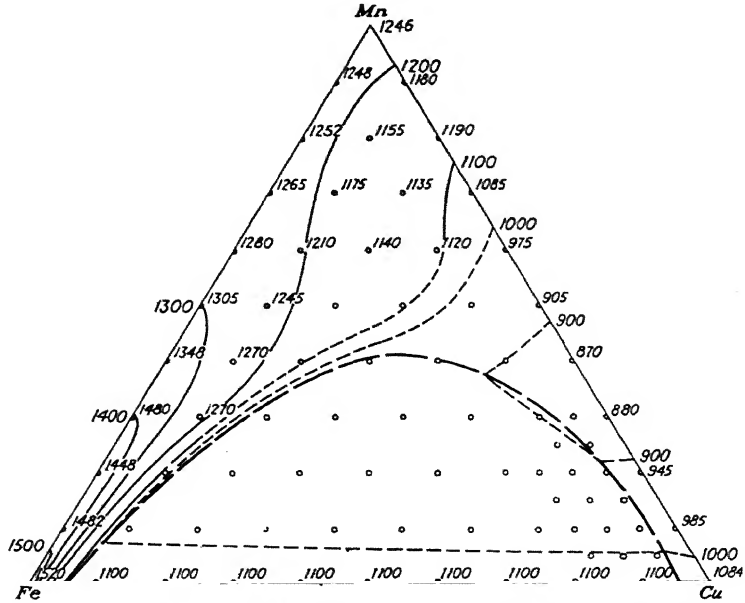


FIG. 149.—Solidus temperatures and isothermal lines in the iron-copper-manganese system. The heavy dashed line outlines the miscibility gap at some unknown temperature. (*Parravano.*[67])

compositions of quaternary alloys. All alloys containing a fixed amount of one component are located on a plane passing through the tetrahedron and parallel to the face opposite the corner indicating the component whose concentration is fixed. Figures 150 to 156 show the liquidus and solidus temperatures for alloys of constant manganese content. They are therefore sections parallel to the iron-nickel-copper side of the tetrahedron. The compositions of the alloys studied are shown by the circles, the figure to the right and above gives the temperature at which solidification began, and that to the right and below gives the

temperature at which solidification was completed. The lines are isothermals for the liquidus.

According to Parravano, nickel-manganese-copper and iron-nickel-manganese alloys form a continuous series of solid solutions. As described above, there is a miscibility gap in the solid for iron-copper-nickel and iron-copper-manganese alloys. The

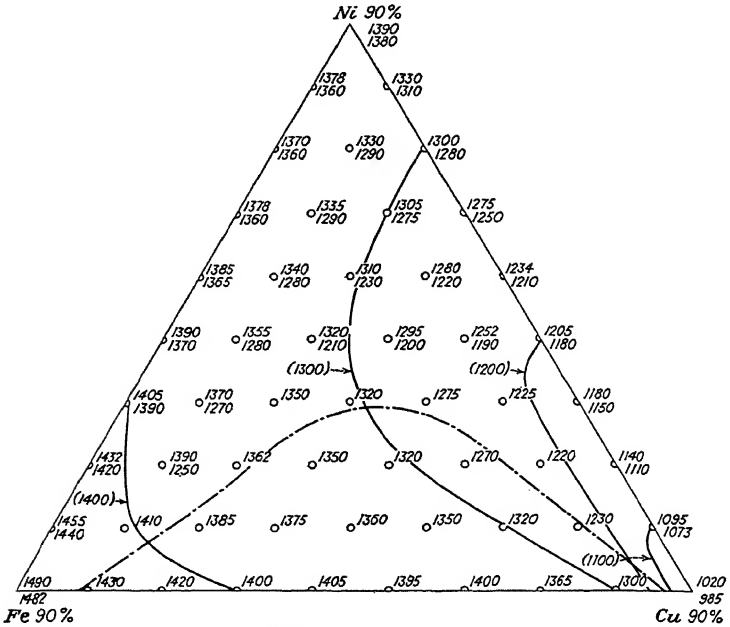


FIG. 150.—Temperatures of beginning and end of solidification for alloys containing 10 per cent manganese. (*Parravano.*[68])

quaternary diagram for temperatures just below complete solidification must be somewhat similar to the sketch shown as Fig. 157. The wedge-shaped space whose edge is *mn* is the two-phase space in which iron-rich and copper-rich alloys are in equilibrium. Alloys outside this space consist of a homogeneous solid solution.

151. Iron-copper-manganese-carbon Alloys.—Ostermann[158] concluded that the miscibility gap in the iron-copper system did not intersect the liquidus but that the addition of a small amount of carbon caused the immiscibility region to intersect the liquidus. Furthermore, the addition of manganese to iron-copper alloys

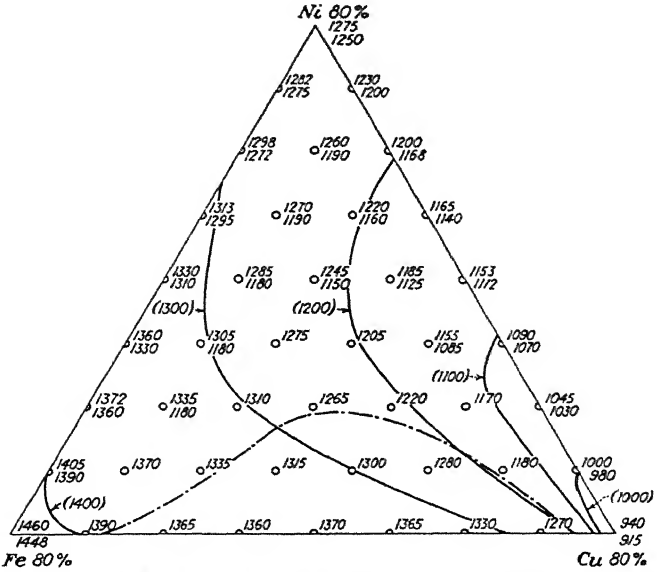


FIG. 151.—Temperatures of beginning and end of solidification for alloys containing 20 per cent manganese. (*Parravano.*[68])

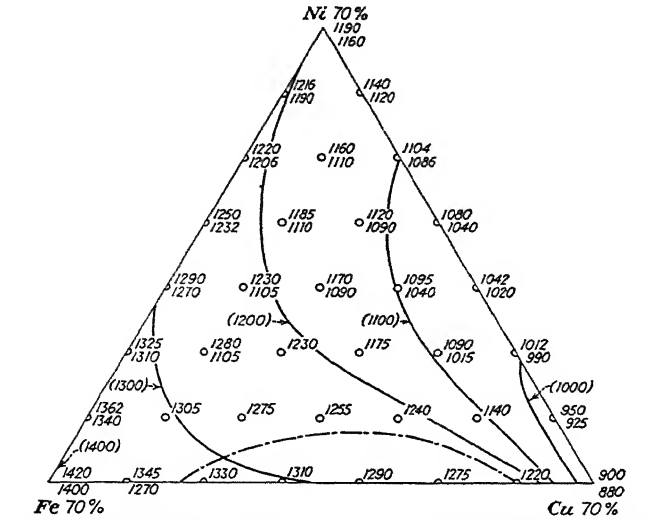


FIG. 152.—Temperatures of beginning and end of solidification for alloys containing 30 per cent manganese. (*Parravano.*[68])

containing small amounts of carbon would tend to cause a contraction of the miscibility gap. In order to test these conclusions he attempted to determine the extent of the liquid immiscibility field in iron-copper-manganese alloys containing small amounts of

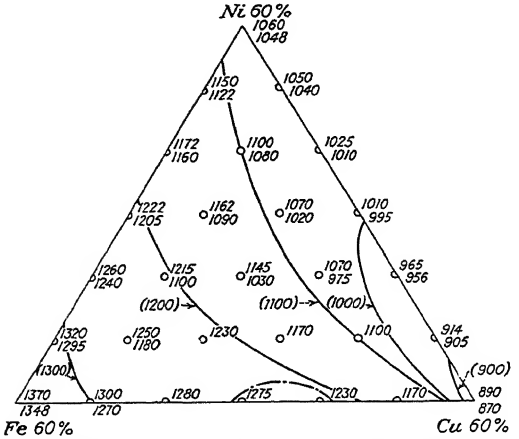


FIG. 153.—Temperatures of beginning and end of solidification for alloys containing 40 per cent manganese. (*Parravano.*[68])

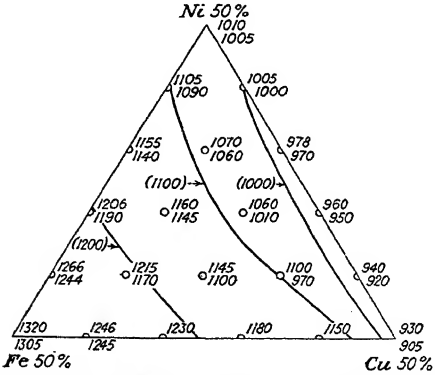


FIG. 154.—Temperatures of beginning and end of solidification for alloys containing 50 per cent manganese. (*Parravano.*[68])

carbon. He used alloys containing 0.1, 0.18, 0.22, 0.4, 0.8, and 1.0 per cent carbon, located according to composition along the lines in the iron-copper-manganese diagram which connect (1) the iron corner and the point at 33 per cent manganese and 67 per cent copper, and (2) the manganese corner and the middle

of the iron-copper side. The alloys were heated to just above the liquidus and examined microscopically after cooling. Some

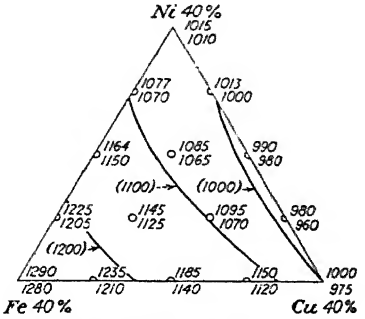


FIG. 155.—Temperatures of beginning and end of solidification for alloys containing 60 per cent manganese.

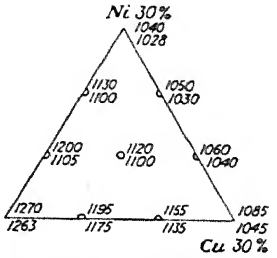


FIG. 156.—Temperatures of beginning and end of solidification for alloys containing 70 per cent manganese. (*Parra-*

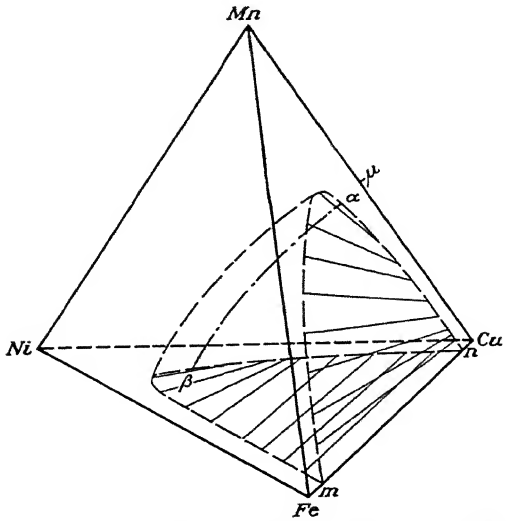


FIG. 157.—Iron-copper-nickel-manganese diagram. (*Parrava*

difficulty was encountered in determining whether the duplex structure in some of the alloys resulted from separation of two liquid phases or the formation of two phases on cooling. In some of the manganese-rich alloys the two liquid phases appeared

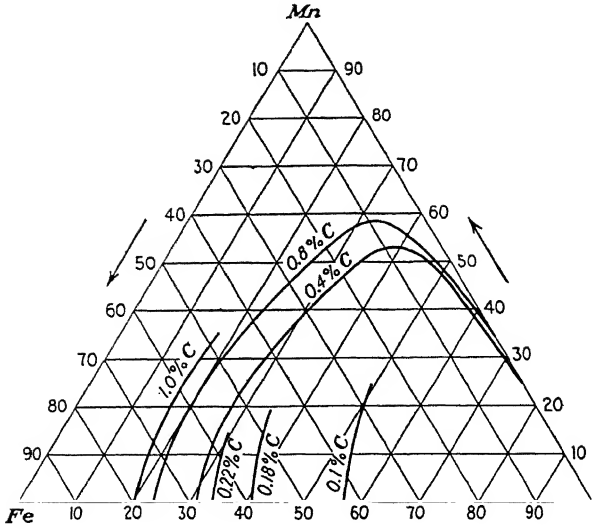


FIG. 158.—Region of liquid immiscibility in iron-copper-manganese-carbon alloys. (*Ostermann.*[158])

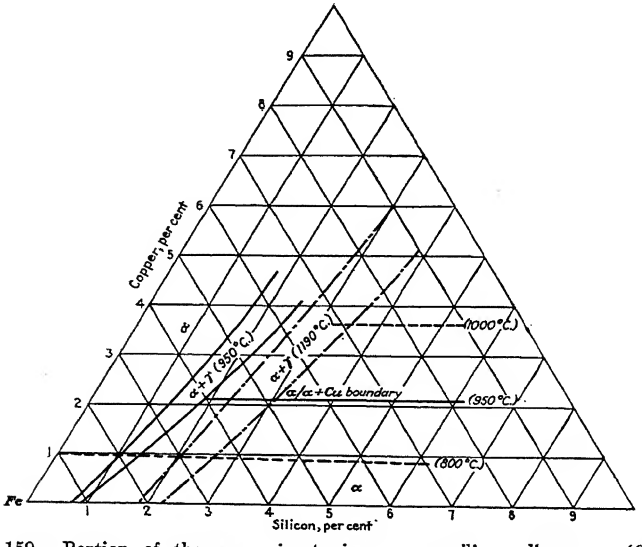


FIG. 159.—Portion of the approximate iron-copper-silicon diagram. (*Smith and Palmer.*)

to differ little in density, for they did not separate into layers. The regions of liquid immiscibility as reported by Ostermann are outlined in Fig. 158. According to these curves, small amounts of carbon have a marked effect in that they greatly widen the field of liquid immiscibility, but small amounts of manganese do not appreciably contract this region. With large amounts of manganese the region of liquid immiscibility is contracted, and the alloys become completely miscible when the manganese exceeds a certain concentration, which depends on the carbon content.

152. Iron-copper-silicon Alloys.—In order to study precipitation hardening in iron-copper alloys containing sufficient silicon to raise the allotropic transformation point to a temperature at which considerable quantities of copper would be dissolved, Smith and Palmer* prepared a group of iron-copper-silicon alloys. From the microstructures of these alloys the approximate diagram shown in Fig. 159 was constructed. The lines shown have not been accurately located, for the compositions varied in steps of 1 per cent. The diagram shows the limits of the alpha-plus-gamma field at 950 and 1190°C. and the lines representing the solubility limit of copper in alpha phase at 800, 950, and 1000°C. The solubility limit of copper in alpha iron at 800°C. is approximately 1.0 per cent; in those alloys containing sufficient silicon to suppress the gamma phase the solubility is approximately 4 per cent at 1000°C. and well over 5 per cent at 1190°C.

Smith and Palmer found that only those alloys lying within a limited range near the iron-rich corner of the iron-copper-silicon diagram could be forged. The limit of forgeability is roughly defined by a concave line drawn from 7 per cent copper to 5 per cent silicon.

Precipitation-hardening studies indicated that silicon had little influence on the hardness increase brought about by precipitation, but that the hardness of the quenched alloys increased with the silicon content. As for the simple iron-copper alloys the maximum increase in hardening due to precipitation was reached with 1 per cent copper. The increased supersaturation with copper, therefore, did not result in increased hardening on precipitation. The tensile properties of some iron-copper-silicon alloys are given in Table 30 (pages 160–162).

* Unpublished report, Anaconda Copper Company.

The copper-rich corner of the copper-iron-silicon diagram was recently studied by Hanson and West.[392]

153. Silicon, Aluminum, and Cobalt in Iron-copper-carbon Alloys.—A series of iron-rich alloys containing approximately 0.8 per cent carbon was used by Roll[373] in determining a portion of the line separating the single-phase field from the polyphase field in iron-copper-silicon alloys. His results are shown in Fig. 160; alloys to the right of the curve contained a copper-rich phase, while those to the left of the curve did not.

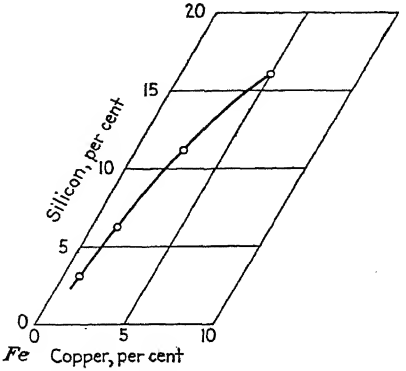


FIG. 160.—Limit of existence of the copper-rich phase in iron-copper-silicon alloys containing 0.8 per cent carbon. (*Roll.*[373])

In more recent work Roll[374] determined the influence of aluminum and cobalt on the line separating the single-phase field from the polyphase field in iron-copper alloys containing 1.5 per cent carbon. With 30 per cent aluminum the line passed through the point representing 24 per cent copper and with 30 per cent cobalt it passed through the point representing 10 per cent copper.

154. Iron-copper-lead Alloys.—Guertler and Menzel[141] melted together almost equal portions of iron, copper, and lead in a graphite crucible and found that three separate liquid layers were formed, wholly consistent with the limited miscibilities of the component binary systems.

B. COPPER IN COMPLEX LOW-ALLOY STEELS

With the exception of the chromium-copper steel developed in Germany, copper-containing low-alloy steels have not been used extensively. However, some data have been obtained on the

properties of steels containing copper in addition to small amounts of other alloying elements and these will be reviewed below.

155. Copper-nickel Steels.—An investigation reported by Colby,[31] in 1899, afforded evidence that the presence of as much as 0.08 per cent copper in a 3 per cent nickel steel used for producing bicycle tubing did not adversely affect the hot- or cold-working properties of the steel.

The most commonly used nickel steels contain approximately 3.5 per cent nickel (S.A.E. 2300 series). As nickel is more expensive than copper it would be desirable to replace part of the nickel by copper provided that this could be done without impairing the properties of the material. Another possible advantage would be in allowing the use of a nickel-copper alloy instead of nickel as an addition agent for the steel; nickel and copper occur together in some Canadian ores and it is more economical to obtain nickel-copper alloys from these ores than it is to obtain these metals separately. Such ores also contain appreciable quantities of iron and they can be treated to yield a nickel-copper iron, which can be refined to a nickel-copper steel by means of any of the common steel-making processes. A number of workers have claimed that part of the nickel in steels of the S.A.E. 2300 series can be replaced by copper without affecting the properties of the steel, but, as will be shown below, this has not been definitely proved.

In 1910, Clamer[58] asserted that a steel containing 2.5 per cent nickel and 1 per cent copper was equivalent to a steel containing 3.5 per cent nickel, but he did not cite data to prove that this was true. He did list the mechanical properties of four steels to which from 2 to 4 per cent Monel metal had been added, but he neglected to state the treatment that the steels had received. Mathews, in discussion of Clamer's paper, gave some data on the properties of a low-alloy nickel-copper steel which indicated that copper at least did not adversely affect the properties of the steel. The steel was made in an electric furnace from a nickel-copper pig iron prepared from Canadian ores. Its properties were compared with those of a nickel steel made by the open-hearth process. The analyses of the two steels were:

Steel	Composition, per cent						
				S	Si	Ni	Cu
Ni-Cu.	0.44	0.50	0.013	0.013	0.034	3.62	0.48
Ni....	0.46	0.70	0.021	0.034	0.066	3.36	

TABLE 84.—MECHANICAL PROPERTIES OF A NICKEL AND A NICKEL-COPPER STEEL*

Steel	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.†	Elongation in 2 in., per cent	Reduction of area, per cent
As rolled				
Ni-Cu	115,000	72,400	22	51
Ni	122,000	74,625	16	34
Annealed				
Ni-Cu	107,300	63,750	25	48
Ni	119,000	64,750	17	37.5
Quenched in oil from 815°C. (1500°F.) and tempered at 315°C. (600°F.)				
Ni-Cu	200,000+	185,000	12	46
Ni	200,000+	185,000	2	4
Quenched in oil from 815°C. (1500°F.) and tempered at 425°C. (800°F.)				
Ni-Cu	172,500	154,000	13.25	49.1
Ni	175,000	154,500	9.75	30.8

* Mathews in discussion of paper by Clamer.[58]
† Reported as elastic limit.

Their tensile properties are given in Table 84. In all conditions the nickel-copper steel had the higher values of elongation and reduction of area, but, as Mathews pointed out, this may possibly be attributed to the natural superiority of the electric-furnace steel rather than to the copper content. The presence of copper certainly did not damage the steel.

In a private communication Mathews wrote that the steel mentioned in discussion of Clamer's paper was of considerable historical interest because it was the first electric steel made in this country entirely from ore by electric smelting. The pig iron was smelted direct from cupriferous ores in Canada and refined in the first Héroult furnace operated in this country, which was at the Halcomb Steel Company. Incidentally, the heat of material was very good in all particulars.

Clamer[58] reported tensile values for two nickel-copper steels, which are given here even though the materials can hardly be

classified as "low-alloy" steels. The materials were tested in the as-rolled condition. Their composition and properties were:

Composition and properties	Number 1	Number 2
Copper, per cent	9.00	19.50
Nickel, per cent	22.00	45.00
Carbon, per cent	0.22	0.20
Tensile strength, lb. per sq. in	101,000	98,230
Yield strength, lb. per sq. in	57,300	54,150
Elongation in 2 in., per cent	42.5	35.0
Reduction of area, per cent	61.5	47.9

The *Report of the Royal Ontario Nickel Commission*[84] and articles by Colvocoresses,[87] Leonard,[93] Mason,[89] Morrin,[95] Hardy and Blizard,[99] and Hardy and Bleakney[289] deal with nickel-copper steels made from Canadian ores, and most of these reports contain some data on the properties of such steels. While these data indicate that copper in nickel steel is not deleterious, they do not show that the copper content affected the properties of the steels advantageously; hence there is no point in including these values here.

Forgings from copper-nickel steel made in an electric furnace were tested at Woolwich Arsenal by Jones.[144] Ingot 1 was octagonal and 18 in. wide at both top and bottom; it was forged into a section 9.75 in. in diameter at the top and 12.75 in. at the bottom. Ingot 2 was octagonal and 15 in. wide at both top and bottom; it was forged into a cylinder having a diameter of 8.5 in. Analyses of sections were as follows:

Element	Percentage		
	Bottom end of ingot 1	Top end of ingot 1	Bottom end of ingot 2
Carbon	0.42	0.45	0.48
Silicon	0.20	0.20	0.24
Manganese	0.58	0.63	0.80
Sulphur	0.033	0.038	0.048
Phosphorus	0.015	0.015	0.022
Nickel	2.71	2.74	2.18
Chromium	0.01	0.01	0.01
Copper	0.58	0.59	0.55

The forgings were annealed at 900°C. (1650°F.), quenched in oil from 815°C. (1500°F.), and then tempered for 3 hr. at 665°C. (1230°F.). The transverse properties of the forgings after this treatment are given in Table 85. The impact tests were made on pieces having a 45-deg. V-notch with a root radius of 0.25 mm. (0.01 in.), 2 mm. (0.08 in.) deep. The microstructure showed a thin network of ferrite enclosing sorbite. No flaws or hair cracks were found in any of the sections examined.

Cooling curves made by Jones on steel from forging 1 and on a copper-free steel containing 2.68 per cent nickel indicated that the copper in the forging had no influence on the position of the critical points. The Brinell hardness values of 1 × 1.5-in. sections from forging 1 quenched in water from 900°C. (1650°F.) and tempered for 30 min. at the temperatures shown were:

Tempering temperature, °C.	None	200	300	400	450	500	550	600	650
Tempering temperature, °F	None	390	570	750	840	930	1020	1110	1200
Brinell hardness.....	506	497	450	400	344	318	390	276	244

Properties of 1 × 1.5-in. sections of forging 1 after having received different heat treatments are given in Table 86.

Corrosion tests carried out by immersion in tap water indicated that the corrosion resistance of the nickel-copper steel was a little better than that of carbon steel but somewhat inferior to that of both nickel and nickel-chromium steels.

From the results of his investigation Jones concluded that 0.6 per cent copper in nickel steel was in no way detrimental to the properties but that it produced no beneficial effect even in promoting resistance to corrosion. According to him, in order to give tests equal to those of a 3.5 per cent nickel steel, a nickel-copper steel must contain 3.5 per cent nickel irrespective of its copper content up to 1 per cent.

For the purpose of determining the resistance of nickel-copper steels to sea water Friend and West[286] prepared small melts of the steels whose compositions are listed in Table 87. The small ingots (56 lb.) were annealed at 950°C. (1740°F.) for 2 hr. and samples for corrosion and tensile tests obtained. Portions of the ingots were then forged. Steel 3 was unmachinable even after annealing. Steel 7 was brittle: "one specimen cracked during the pasty stage of cooling, and two others cracked during handling in the vise." The tensile properties of the alloys are given

TABLE 85.—TRANSVERSE PROPERTIES OF LARGE HEAT-TREATED FORGINGS OF NICKEL-COPPER STEELS*

Forging number	Location of specimen	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.†	Elastic limit, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Izod impact, ft-lb.	Brinell hardness
1	Bottom	93,200	56,400	52,000	25	49	23	188 to 201
	Middle	99,200	64,300	60,000	11	23	27	197 to 203
	Top	100,400	61,800	49,000	10	23	22	205 to 207
2	Bottom	98,800	62,000	56,000	21	41	20	201 to 206
	Top	99,500	61,600	54,000	22	43	18	203 to 208

* Jones.[144]

† Stress for permanent extension of 0.2 per cent.

TABLE 86.—PROPERTIES OF A HEAT-TREATED NICKEL-COPPER STEEL*

Tempering temperature		Tempering time, hr.	Cooled	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Izod impact, ft-lb.	Brinell hardness
°C.	°F.									
Quenched in oil from 1000°C. (1830°F.)										
650	1200	2	Water	103,300	69,400	54,000	20	43	33	221
650	1200	..	Slowly	102,400	72,800	63,000	20	42	25	217
Quenched in oil from 900°C. (1650°F.)										
670	1240	2	Air	99,000	65,200	52,000	23	52	35	206
650	1200	2	Water	106,200	78,800	63,000	19	39	30	223
650	1200	2	Slowly	103,500	73,500	65,000	22	50	25	216
650	1200	6	Air	102,400	73,700	63,000	20	42	30	213
600	1110	2	Air	111,100	77,500	65,000	19	42	25	228
550	1020	2	Air	126,300	97,000	76,000	16	42	22	257
Quenched in oil from 820°C. (1510°F.)										
650	1200	2	Air	103,900	73,000	65,000	22	47	33	217
600	1110	2	Air	111,100	75,700	67,000	20	46	26	226
550	1020	2	Air	125,400	93,600	78,000	14	34	24	257

* Jones.[144]

† Stress for permanent extension of 0.2 per cent.

in Table 88; those described as "annealed" had not been forged. Bars used in the corrosion tests were 1.125 in. square, 9 in. long, and were machined all over. They were fixed in a pitch-pine frame and exposed at half-tide level. After an exposure of 2 years they were removed and the corrosion loss was determined by scraping away the corrosion products and weighing. The results of the corrosion tests are shown in Table 89. It was concluded that the presence of copper in amounts up to 3.70 per cent increased the resistance to intermittent action of the sea.

TABLE 87.—COMPOSITION OF STEELS MADE BY FRIEND AND WEST[286]

Number	Composition, per cent						
	C	Mn	Si	S	P	Ni	Cu
1	0.28	0.69	0.28	0.03	0.037	3.75	1.16
2	0.20	0.58	0.25	0.02	0.029	3.44	2.35
3	0.18	0.55	0.20	0.028	0.031	3.90	3.58
4	0.16	0.63	0.33	0.022	0.027	0.26	1.13
5	0.18	0.53	0.33	0.036	0.022	0.26	2.44
6	0.23	0.58	0.24	0.036	0.036	0.40	3.70
7	0.21	0.52	0.30	0.018	0.022	3.80	9.84
8	0.25	0.61	0.44	0.026	0.026	0.34	0.00

TABLE 88.—MECHANICAL PROPERTIES OF NICKEL-COPPER STEELS*

Number	Condition	Composition, per cent		Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.†	Elongation in 3 in., per cent	Reduction of area, per cent
		Cu	Ni				
8	Annealed	....	0.34	82,000	53,800	18	24.0
8	Forged	....	0.34	86,500	54,700	28	52.5
4	Annealed	1.13	0.26	73,300	55,100	26	40.0
4	Forged	1.13	0.26	78,400	57,800	26	43.0
5	Annealed	2.44	0.26	82,000	63,600	17	28.0
5	Forged	2.44	0.26	109,800	82,900	18	45.0
6	Annealed‡	3.70	0.40	53,800	.....	3	4.5
6	Forged	3.70	0.40	106,400	87,000	20	41.5
1	Annealed‡	1.16	3.75	100,800	71,200	2	4.5
1	Forged	1.16	3.75	152,300			
2	Annealed	2.35	3.44	114,200	88,700	15	20.0
2	Forged	2.35	3.44	197,700	.....	8	24.0
7	Annealed‡	9.84	3.80	13,400			

* Friend and West.[286]
† Reported as yield point.
‡ Unsound bar.

TABLE 89.—CORROSION OF COPPER-NICKEL STEELS IN SEA WATER*

Composition, per cent		Condition	Loss in weight, g.	Relative loss in weight for equal areas	Depths of deepest pits		Remarks
Cu	Ni				Sides, mm.	Ends, mm.	
....	0.34	Annealed	41.34	104 } 100	0.64, 0.28	0.45	Surfaces pinholed, otherwise good. Slight corrosion where bars entered frame
		Annealed	36.25	96 }	0.32	0.50	
		Forged	35.70	89.3	0.15, 0.54	0.84	
1.13	0.26	Annealed	38.73	100.1	.....	0.95	Slight pitting on faces. Ends locally attacked
		Forged	28.88	108.1	.....	.....	Round bar, uniformly attacked
2.44	0.26	Annealed	36.36	96.0	0.41, 0.51	0.44, 0.33	Sides and ends pitted
		Forged	39.25	93.3	0.47, 0.69	0.30	
3.70	0.40	Annealed	34.58	88.3	0.48, 0.23	0.51, 1.33	Localized corrosion on every side and at ends
		Forged	37.42	96.4	0.39, 0.40	1.05	
1.16	3.75	Annealed	20.33	52.4	.....	0.61, 0.62	Excellent. Ends only attacked
		Forged	22.90	53.7	.....	0.39, 0.87	Tendency on one face to pit. Ends attacked
2.35	3.44	Annealed	26.75	68.5	0.45	0.50, 0.78	Slight pitting on several faces and localized corrosion at ends
		Annealed	27.45	71.0	.....	0.69, 0.50	
		Forged	45.42	113.0	0.27	0.93, 0.32	
9.84	3.80	Annealed	27.08	75.5	.....	0.75, 0.85	Slight pitting on several faces and localized corrosion at ends

* Friend and West.[286]

156. Nickel-chromium-molybdenum Die Steels.—Some interest is being shown in the replacement of the bulk of the nickel in the nickel-chromium-molybdenum steels of the general type mentioned on page 306 of "The Alloys of Iron and Molybdenum." While no data are available as yet, some workers consider this replacement to be quite feasible.

157. Copper in Silicon Steels.—A structural steel that was used in Germany, according to Petersen,[242] had the following composition:

	Percentage
Carbon	0.15 to 0.2
Manganese	Approximately 0.6
Silicon	0.8 to 1.0

In the as-rolled condition it had a minimum tensile strength of 68,000 lb. per sq. in., a minimum yield strength of 51,000 lb. per sq. in., and an elongation of at least 20 per cent. The high silicon content tended to lower the corrosion resistance, but this was counteracted by the addition of from 0.2 to 0.3 per cent copper. This small amount of copper, according to Petersen, had no influence on the mechanical properties. It did, however, increase the resistance to attack by dilute acids, which was taken as being indicative of an increased corrosion resistance. The silicon steel containing small amounts of copper was superseded, to some extent at least, by chromium-copper and manganese-silicon-copper steels containing more copper, the copper in these steels seeming to increase both strength and corrosion resistance. These steels will be discussed in the next section.

The composition and properties of a low-alloy steel made by Krupp and studied by Pomp and Hempel[368] were:

Carbon, per cent	0.13
Silicon, per cent	0.40
Manganese, per cent	1.22
Copper, per cent	0.39
Chromium, per cent	0.04
Tensile strength, lb. per sq. in	74,800
Yield strength, lb. per sq. in	51,400
Elongation, per cent	24.7
Reduction of area, per cent	51.4

Cast silicon steels were investigated by Schulz and Bonsmann,[270] who prepared a series of castings containing from 0.14 to 0.18 per cent carbon, from 0.7 to 1.2 per cent manganese, and from 0.7 to 1.3 per cent silicon. One of these steels contained

0.30 per cent copper. The silicon steels were less resistant to attack by dilute acids than steels of normal silicon content, but the copper-bearing silicon steel was more resistant than ordinary steel. The copper had no measurable influence on the mechanical properties. Some of the Russian steels made from Ural pig iron contain between 0.10 and 0.15 per cent copper.[305]

Kussmann, Scharnow, and Messkin[265] suggested that it might be desirable to add small amounts of copper to silicon steels

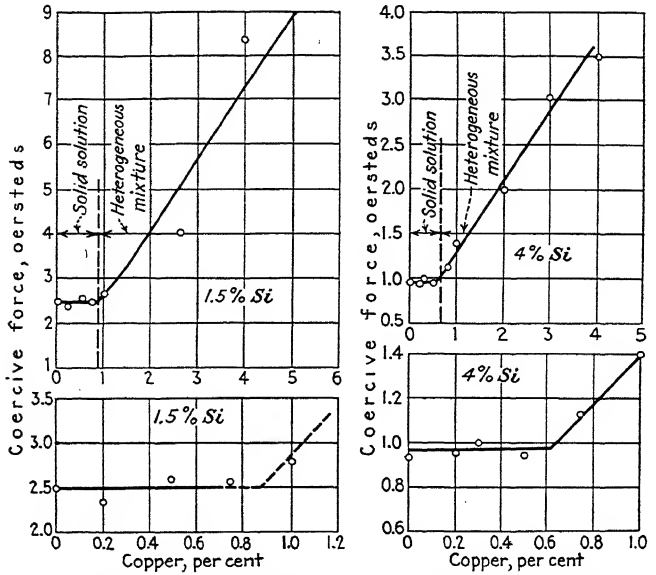


FIG. 161.—Influence of copper content on the coercive force of silicon steels. (*Kussmann, Scharnow, and M*

used for magnetic purposes in order to increase corrosion resistance. Copper in amounts below the limit of solid solubility should not adversely influence the magnetic properties. In order to determine the effects of small amounts of copper in silicon steels two series of steels containing respectively 1.5 and 4 per cent silicon and different amounts of copper were prepared in a high-frequency furnace. The alloys were forged into cylindrical rods and annealed at 875°C. (1505°F.) for 7 hr. The coercive force of the annealed alloys is shown in Fig. 161. As is indicated by the curves, the limit of solubility of copper was about 0.9 per cent in the 1.5 per cent silicon steel and about

0.6 per cent in the 4 per cent silicon steel. Induction for different magnetizing forces, expressed in ampere turns per centimeter, and maximum permeability are shown in Figs. 162 and 163. These figures together with Fig. 161 show that copper in amounts that enter into solid solution, less than 0.6 or 0.9 per cent, has no detectable influence on the magnetic properties of silicon steels. The values for maximum permeability of the 4 per cent silicon steel vary widely, but there is no reason for attributing the irregu-

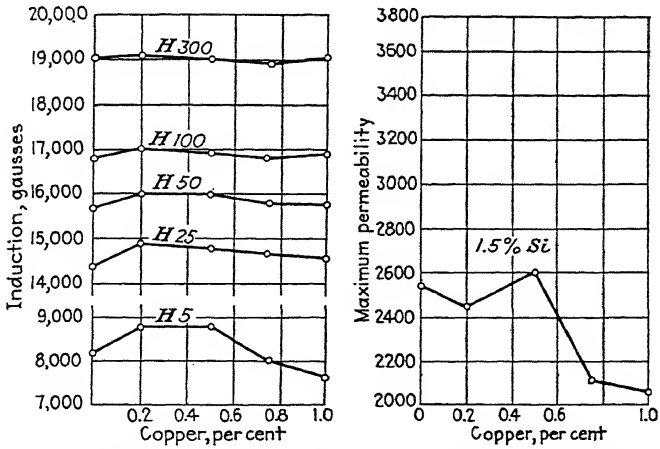


FIG. 162.—Influence of copper content on the induction and maximum permeability of steels containing 1.5 per cent silicon. (*Kussmann, Scharnow, and*

larity to copper. Electric-resistance measurements proved that copper in amounts up to 1 per cent did not affect the resistance and therefore showed that small amounts of copper would not influence core loss. Rockwell *B* hardness values of the alloys are shown in Fig. 164. Samples of the alloys were immersed in a 25 per cent solution of sulphuric acid for 20 hr. and weight loss was determined. Copper even in amounts below the solubility limit decreased the weight loss, which led the authors to conclude that copper appreciably increased the corrosion resistance of the steels.

In a book on stainless steels[381] DeVries wrote as follows:

Silicon and copper both have great "affinity" for each other and for iron. This can best be illustrated in chromium-free alloys. Thus, it is well known that "electrical sheet," a low-carbon silicon steel (3 or 4

per cent Si) is a comparatively brittle material, not very easy to produce, but when this same alloy has from 1.5 to 2.0 per cent of copper added, the combination has none of the disadvantages in melting, forging, and rolling associated with high silicon alone.

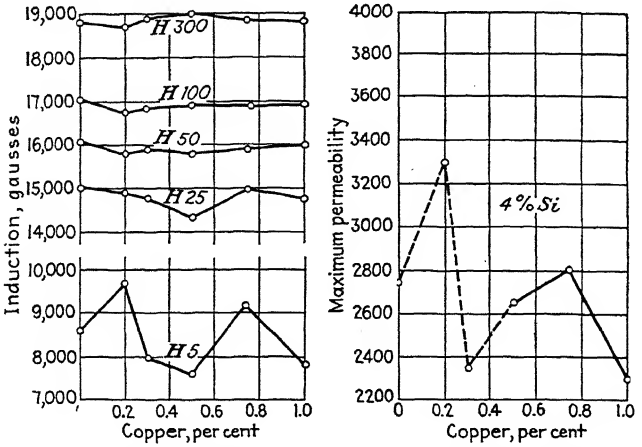


FIG. 163.—Influence of copper content on the induction and maximum permeability of steels containing 4 per cent silicon. (*Kussmann, Scharnow, and*)

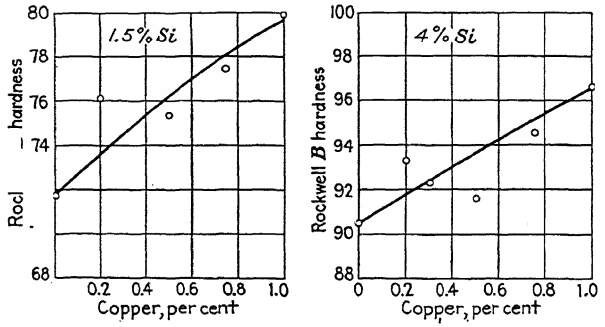


FIG. 164.—Influence of copper content on Rockwell *B* hardness of silicon steels. (*Kussmann, Scharnow, and Messkin.*[265])

158. Copper-chromium Steels.—The copper-chromium structural steel now used in Germany was first described by Schulz,[215] who gave evidence to support the contention that this steel was at least as good as the silicon steel which it was to supplant.

According to Petersen,[242] the silicon structural steel mentioned above had the disadvantage that as the size of section

increased the yield strength of the as-rolled material decreased appreciably. A high-strength cheap structural steel was then developed which contained a small amount of chromium, less silicon, and sufficient copper to bring about increased strength. The approximate analysis of this steel was:

	Percentage
Carbon	0.15
Silicon	0.25
Copper	0.50 to 0.80
Chromium	0.40

Small sections of this steel had substantially the same properties as the silicon steel and the decrease in yield strength with increased size of section was less pronounced. Like the silicon steel, this steel was primarily developed for use in the as-rolled condition. The requirements for such a steel are that the tensile and yield strength be higher than for carbon steel of the same carbon content and that the ductility shall not be appreciably lower than that of the carbon steel. The steel shall be one that can be easily manufactured by large-scale production methods, and its cost shall be less than that of the well-known nickel steel containing approximately 3 per cent nickel. As judged by recent literature, German metallurgists apparently find that the copper-chromium steel fulfills these desiderata. Frequency* curves of tensile strength, elongation, and yield strength of the copper-chromium steel fabricated into different sections in commercial production are shown in Fig. 165. Maxima were found for a tensile strength of 82,500 lb. per sq. in., an elongation of 24 per cent, and a yield strength of 57,000 lb. per sq. in. Another steel of essentially the same properties, according to Petersen, contains:

	Percentage
Carbon	0.15
Silicon	0.50
Manganese	1.1 to 1.5
Copper	0.3 to 0.6

Frequency curves for the properties of this steel are shown in Fig. 166.

In a recent article Koppenberg[323] discussed low-cost structural steels with particular reference to their use in bridge con-

* Statistical curves showing the frequency of the occurrence of the various values.

struction and pointed out that extensive studies had indicated that the properties of such steels were equal to those of 3 per cent

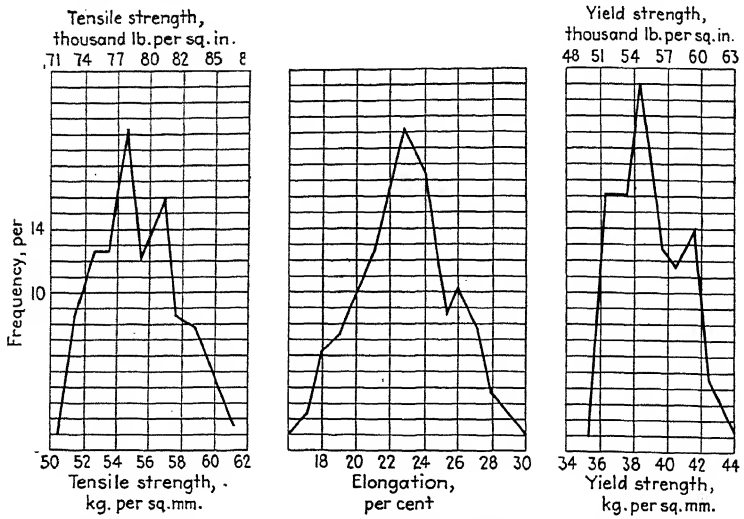


FIG. 165.—Frequency curves for mechanical properties of copper-chromium structural steels. (*Petersen.*[242])

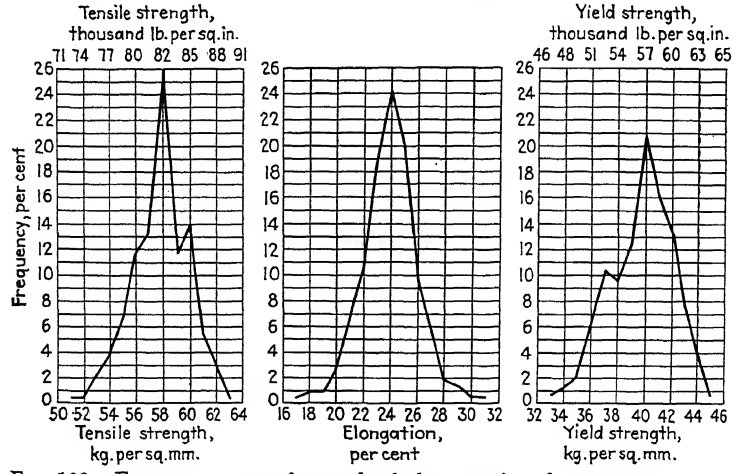


FIG. 166.—Frequency curves for mechanical properties of manganese-copper-silicon steels. (*Petersen.*[242])

nickel steels. The steels referred to are designated as St. 52 in Germany. The numeral refers to the minimum tensile strength

of 52 kg. per sq. mm. (74,000 lb. per sq. in.). The approximate composition of steels of this class is given by Koppenberg[323] and Gerritsen and Schoenmaker[349] in Table 90.

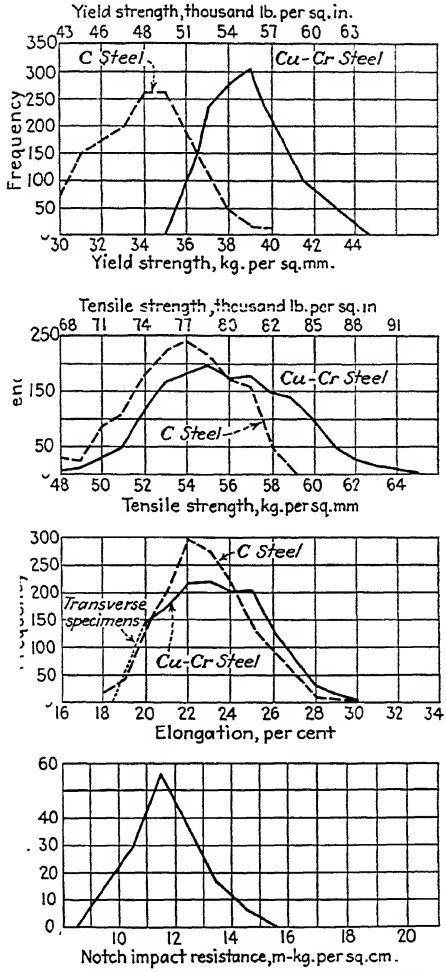


FIG. 167.—Properties of copper-chromium structural steels as determined by analysis of 1,500 tests. (*Schulz and Buchholtz.*[249])

The properties of the German copper-chromium structural steel were discussed at length by Schulz and Buchholtz.[249] They gave the frequency curves shown in Fig. 167, which show

TABLE 90.—COMPOSITION OF GERMAN HIGH-STRENGTH STRUCTURAL STEELS (ST. 52) CONTAINING FROM 0.12 TO 0.25 PER CENT CARBON*

Designation	Composition, per cent				
	Si	Mn	Cu	Cr	Mo
Silicon steel with normal copper	0.8 to 1.1	0.75 to 0.9	0.25 to 0.4		
Lauchhammer structural	0.5 to 0 7	0.9 to 1.1	0.5 to 0.6		
Krupp.	0.3 to 0.5	1.2 to 1.6	0.3 to 0.6		
Union structural	0.3 to 0.5	0.7 to 1.0	0.6 to 1.0	0.4 to 0.6	
GHH.....	To 0.5	1.0 to 1.3	Over 0.35		0.15 to 0.25

* Koppenberg[323]; Gerritsen and Schoenmaker.[349]

the results of fifteen hundred individual tests on copper-chromium steels. The figure also shows frequency curves for the properties of a carbon steel (St. 48) supposed to have a minimum tensile strength of 48 kg. per sq. mm. (68,000 lb. per sq. in.); this steel differs from the copper-chromium steel chiefly in that it has a lower yield strength. The properties of forgings of several sizes made from two different heats of the copper-chromium steel are listed in Table 91. The values show that the properties are not

TABLE 91.—AVERAGE PROPERTIES OF FORGINGS MADE FROM COPPER-CHROMIUM STRUCTURAL STEEL*

Heat	Diameter		Elongation in forging	Treatment†	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, $l = 10d$, per cent	Reduction of area, per cent	Charpy impact, m-kg. per sq. cm.
	mm.	in.							
A	230	9.0	4	F	74,000	50,000	20	58	8
				A	77,000	48,000	24	67	12
	100	3.9	25	F	77,000	51,000	23	67	14
				A	75,000	51,000	25	66	13
B	250	9.8	3.8	F	88,000	54,000	19	62	
				A	91,000	58,000	20	62	8
	200	7.9	5.8	F	85,000	53,000	21	53	8
				A	84,000	51,000	21	61	8
	155	6.1	10	F	84,000	51,000	20	59	8
				A	85,000	55,000	24	63	7
	100	3.9	23	F	84,000	54,000	..	..	11
				A	85,000	55,000	21	64	9

* Schulz and Buchholtz.[249]

† F—forged; A—forged and annealed at 850°C. (1560°F.).

appreciably changed in either the as-forged or annealed condition as the section changes. According to the investigators, the yield strength of these large forgings is 7,000 lb. per sq. in. higher than is to be expected in carbon steels. The copper-chromium steel was found to weld satisfactorily, and the strength of the welded steel was at least 85 per cent that of the original material. One sample of the annealed steel had an endurance limit of between 40,000 and 41,000 lb. per sq. in., which gave an endurance ratio between 0.46 and 0.47. Notched-bar impact tests at tempera-

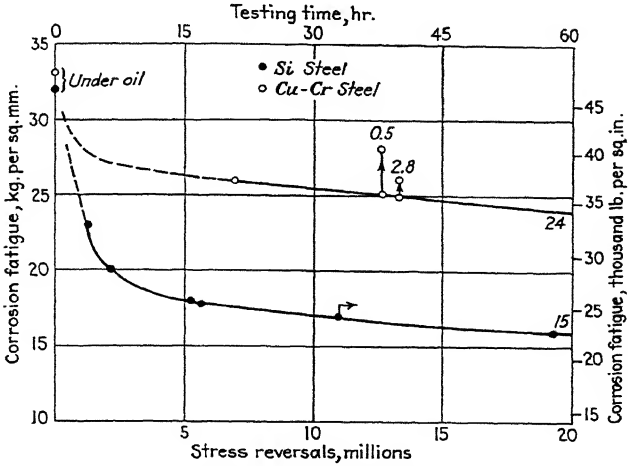


FIG. 168.—Endurance curves for a silicon and a copper-chromium structural steel tested in tap water. (*Schulz and Buchholtz.*[303])

tures between −80 and 300°C. (−110 and 570°F.) on samples compressed to a reduction in height of 10 per cent and heated to 250°C. (480°F.) indicated that the room-temperature impact resistance of the copper-chromium steel was less affected by aging than carbon steel; copper and chromium tended to cause the steep portion of the impact-resistance-versus-temperature curve to move toward lower temperatures.

In another article, Schulz and Buchholtz[303] gave some data indicating that the copper-chromium steel had a comparatively good resistance to corrosion fatigue. Figure 168 shows stress-cycle curves for a silicon and a copper-chromium steel tested in tap water. When tested in oil the former steel had an endurance limit of 45,000 lb. per sq. in. and the latter 47,000 lb. per sq. in.

As the curves show, the corrosion-fatigue properties of the copper-chromium steel in tap water were much the better, apparent corrosion-fatigue limits being 21,000 lb. per sq. in. for the silicon steel and 34,000 lb. per sq. in. for the other steel.

In studying the susceptibility to embrittlement of structural steels Rötscher and Fink[333] used five steels of the compositions listed in Table 92. The two carbon steels, Nos. 1 and 2, were heated to 930°C. (1705°F.) and cooled in air; the other steels were

TABLE 92.—ANALYSIS OF STEELS USED IN AGING STUDY*

Steel		Composition, per cent					
Number	Type	Si	Mn	S	Cu	Cr	
04	Basic Bessemer	0.01	0.37	0.066	0.046	0.09	
15	Basic open-hearth	0.01	0.57	0.024	0.030	0.18	
15	Si	0.89	1.12	0.053	0.036	0.1	
15	Cu-Cr	0.36	0.87	0.022	0.026	0.85	0.51
19	Cu-Mn-Si	0.5	1.09	0.016	0.025	0.60	

* Rötscher and Fink.[333]

TABLE 93.—PROPERTIES OF STEELS BEFORE AND AFTER "AGING" TREATMENT*

Steel		Treatment†	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, $l = 10d$, per cent	Reduction of area, per cent	Brinell hardness, 5/750/30
Number	Type						
1	Basic Bessemer	A	60,200	46,000	31.2‡	67.2	121
		B	84,600	76,400	16.5‡	54.1	156
2	Basic open-hearth	A	59,400	34,700	30.6	65.3	105
		B	75,800	71,800	9.7	59.4	148
3	Si	A	75,400	52,100	28.8	65.1	148
		B	91,700	79,900	9.2	56.5	193
4	Cu-Cr	A	76,000	53,100	25.8	65.8	153
		B	88,900	84,400	8.3	59.9	189
5	Cu-Mn-Si	A	78,800	51,700	25.5	61	145
		B	90,700	77,500	7.7	54.9	190

* Rötscher and Fink.[333]
† A—annealed; B—aged.
‡ $l = 5d$.

furnace cooled from 850°C. (1560°F.). In order to determine the susceptibility to embrittlement, bars with a cross-section of 10 × 11 mm. (0.39 × 0.43 in.) and 100 mm. (3.9 in.) long were deformed by compression so that the 11-mm. dimension became 10 mm., which produced a reduction in thickness of 9.1 per cent. The cold-worked samples were then heated to 250°C. (480°F.) for a period of 30 min. The tensile properties and Brinell hardness

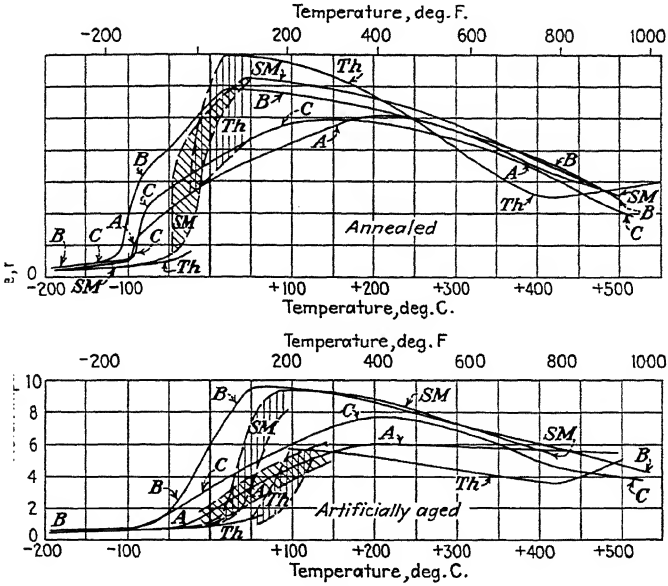


FIG. 169.—Notched-bar impact resistance of annealed and specially treated samples of some structural steels. *Th*, basic Bessemer steel; *SM*, basic open-hearth steel; *A*, silicon steel; *B*, copper-chromium steel; *C*, copper-manganese-silicon steel. (*Rötscher and Fink.*[333])

values of the steels before and after this treatment are shown in Table 93. Charpy impact tests were made on both the annealed and specially treated samples at temperatures from −180 to 500°C. (−290 to 930°F.). The impact specimens had a cross-section of 10 × 10 mm., a keyhole notch and the area at the reduced section was 5 × 10 mm. The results of the impact tests are shown by the curves in Fig. 169. The special treatment, working and heating to 250°C. (480°F.), caused the steep portion of all impact-temperature curves to move to higher temperatures, but both before and after the special treatment the steep portion

of the curve for the copper-chromium steel was at lower temperatures than for the other steels. Of the five steels used, the copper-chromium steel was therefore the least susceptible to embrittlement as judged by the testing method employed. The copper-manganese-silicon steel, No. 5, had an intermediate susceptibility. As is to be expected, the Bessemer steel, No. 1, had the greatest susceptibility to embrittlement. Although not stated in the article, it is probably safe to assume that the low-alloy steels, Nos. 3, 4, and 5, were made by the basic open-hearth process.

During the course of an extended study of the "aging" of soft steels von Köckritz[322] used three copper-chromium steels, one made by the usual process, evidently in the basic open-hearth, and the others by a "special" process. Aging of these steels was studied by elongating 5 per cent, heating to a temperature between 100 and 350°C. (210 and 660°F.), and repeating this procedure until the specimen broke. The stress-strain curves obtained indicated the amount of aging. The two copper-chromium steels made by a special method showed the least amount of aging of any of the 10 steels used, and the other copper-chromium steel had aging characteristics similar to other steels.

Egan, Crafts, and Kinzel[348] found that a steel containing 0.10 per cent carbon, 0.83 per cent chromium, and 0.53 per cent copper had a high impact resistance at subatmospheric temperatures. The Izod values were:

Temperature		Impact resistance, ft-lb. per sq. cm.
°C.	°F.	
20	70	85
− 50	− 60	92
− 80	−110	41
−185	−300	2.5

Franke[285] in discussing boiler steels claimed that the copper-chromium steel had non-aging characteristics.

An extensive study of the endurance properties reported by Buchholtz and Schulz[279] showed that the copper-chromium structural steel had a normal endurance ratio, as determined on the basis of 4 million cycles, and that the endurance ratio was not affected by notches, threads, or holes to a greater degree than in other structural steels, including nickel steel. In fact, evidence

was given that the endurance properties were exactly the same as for a 3 per cent nickel steel. Endurance tests were made in which the stress alternated about a value other than zero, and the results indicated that the behavior under these conditions was also normal.

The copper-chromium structural steel has also been discussed in articles by Buchholtz[228] and Guillet.[261]

The German copper-chromium steel is ordinarily used in the as-rolled condition, but Buchholtz and Köster[257] found that it responds to a precipitation-hardening treatment and that desirable properties are thereby produced. As mentioned in Chapter VI, it is not necessary to quench copper steels in a liquid medium in order to put them in a condition for precipitation hardening, and steels containing more than a certain amount of copper can be hardened by cooling in air from about 800°C. (1470°F.) and reheating to 500°C. (930°F.). According to data reported by Buchholtz and Köster, copper-chromium steels respond to a precipitation-hardening treatment to about the same degree as low-carbon copper steels. One of the steels used by these investigators had the following analysis:

	Percentage
Carbon	0.15
Silicon	0.41
Phosphorus	0.024
Sulphur	0.029
Copper	1.1
Chromium	0.38

The properties of this steel after heating specimens, previously air cooled, to different temperatures for periods of 1 hr. are shown in Fig. 170. The impact values were obtained with a 10 × 10 × 60-mm. Charpy specimen having a key-hole notch 5 mm. deep.

When this steel was heated at approximately 500°C. (930°F.), tensile and yield strength increased perceptibly while elongation, reduction of area, and impact resistance decreased. The impact curve for specimens deformed and then heated to 250°C. (480°F.) indicates that precipitation hardening did not increase the sensitivity of the steel to embrittlement, for the curve is almost parallel to the curve for samples not given this treatment.

Buchholtz and Köster suggested that a precipitation-hardening treatment could be advantageously applied to large sections of

copper-chromium steel. In determining the properties of such sections they used a steel of the following analysis:

	Percentage
Carbon	0.18
Silicon	0.01
Manganese	0.75
Phosphorus	0.036
Sulphur	0.036
Copper	0.87
Chromium	0.42

Ingots weighing approximately 3 tons were forged into rounds 300 mm. (11.8 in.) and 100 mm. (3.9 in.) in diameter, which repre-

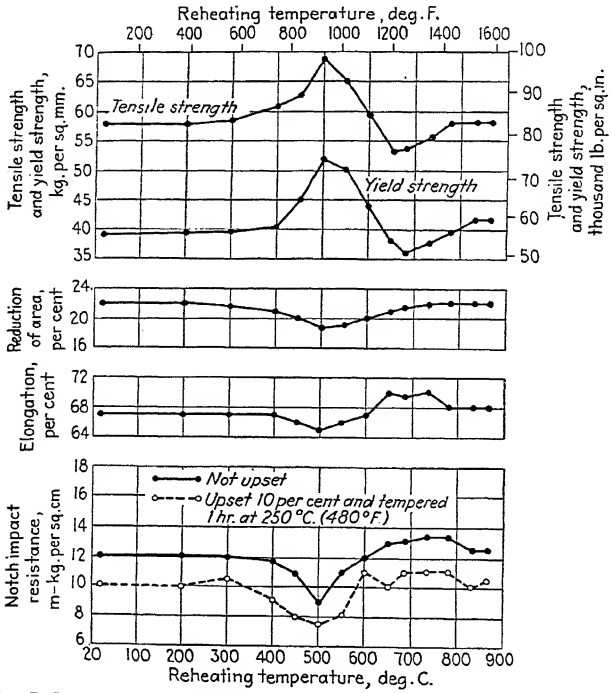


FIG. 170.—Influence of reheating to various temperatures on the properties of air-cooled copper-chromium steel. (*Buchholtz and Köster.*[257])

sented an increase of four and thirty-eight times the length of the ingot. The sections were normalized, and portions were then reheated to 500°C. (930°F.) for a period of 4 hr. The properties

TABLE 94.—PROPERTIES OF LARGE SECTIONS OF HEAT-TREATED COPPER-CHROMIUM STEEL*

Diameter		Position of sample†	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, $l = 10d$, per cent	Reduction of area, per cent	Charpy impact, m-kg per sq. cm.		Endurance limit, lb. per sq. in.‡	Endurance ratio, per cent
Mm.	In.						Normal	Treated		
Normalized										
300	11.8	SL	72,600	51,200	24	70	10.6	10.0	39,800	55
		CL	71,150	48,400	25	69	11.9	10.6		
		CT	69,700	47,000	18	37	7.3	5.0	34,200	48
100	3.9	SL	74,000	52,700	26	69	11.9	10.7		
		CL	72,600	51,200	26	69	10.8	9.5	39,800	55
Normalized and reheated to 500°C. (930°F.) for 4 hr.										
300	11.8	SL	84,000	64,000	18	66	10.6	6.7	51,200	61
		CL	82,500	62,600	19	59	9.5	6.0		
		CT	76,800	59,800	13	36	5.0	2.5	44,100	57
100	3.9	SL	85,400	66,900	21	65	9.3	7.4		
		CL	84,000	66,900	22	65	9.0	6.5	52,700	63

* Buchholtz and Köster.[257]

† S—near surface; C—near center; L—longitudinal; and T—transverse.

‡ Based on 6 million cycles.

TABLE 95.—PROPERTIES OF A COPPER-CHROMIUM STEEL CONTAINING 0.19 PER CENT CARBON, 0.75 PER CENT MANGANESE, 1.02 PER CENT COPPER, AND 0.64 PER CENT CHROMIUM*

Treatment	Quenched		Medium	Reheated		Hours	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, $l = 10d$, per cent	Reduction of area, per cent	Impact resistance, m-kg. per sq. cm.	Endurance limit, lb. per sq. in.	Endurance ratio, per cent
	°C.	°F.		°C.	°F.								
1	860	1580	Air	...	....	..	79,700	55,300	24.5	72	17.2	48,000	60
2	860	1580	Air	480	895	4	102,600	86,200	19.1	66	12.3	61,000	59
3	850	1560	Water	300	570	4	142,300	112,800	8.6	44	5.7	68,000	48
4	850	1560	Water	480	895	1	127,600	114,900	12.9	61	12.1	68,000	53
5	850	1560	Water	600	1110	2	95,400	87,800	17.8	75	21.0	61,000	64

* Lequis, Buchholtz, and Schulz.[361]

both before and after reheating to the aging temperature of 500°C. (930°F.) are given in Table 94. The impact values for the "treated" material are for specimens compressed by 10 per cent and then heated to 250°C. (480°F.). Even the larger section was benefited by heat treatment and the effects of the precipitation-hardening treatment were uniform throughout the entire cross-section.

Table 95 gives the properties of a copper-chromium steel studied by Lequis, Buchholtz, and Schulz.[361] The material was of the following composition and had been rolled to a diameter of 24 mm. (0.95 in.):

	Percentage
Carbon	0.19
Silicon	0.01
Manganese	0.75
Phosphorus	0.029
Sulphur	0.020
Copper	1.02
Chromium	0.64

The impact-resistance values of this steel at different temperatures are given in Table 96, which shows that the material has exceptionally high values at subatmospheric temperatures.

TABLE 96.—IMPACT RESISTANCE OF A COPPER-CHROMIUM STEEL AT DIFFERENT TEMPERATURES*

Treatment†	Impact resistance in m-kg. per sq. cm. at						
	−80°C. (−110°F.)	−50°C. (−60°F.)	−20°C. (−5°F.)	0°C. (30°F.)	+20°C. (+70°F.)	+50°C. (+120°F.)	+100°C. (+210°F.)
1	10.7	10.7	18.6	18.9	17.2		
2	3.2	5.0	5.0	7.0	12.3	16.0	17.8
3	3.3	5.0	4.8	6.0	5.7	7.7	8.0
4	5.0	5.0	8.8	11.9	12.1	13.9	12.7
5	14.8	16.3	17.0	18.3	21.0	20.4	18.0

* Lequis, Buchholtz, and Schulz.[361]
† See preceding table for treatment.

In U. S. Patent 1,957,427 of May 8, 1934, Buchholtz shows that the tensile and yield strength and elongation of cold-worked copper-chromium steels may be increased by heating to a temperature that will bring about precipitation hardening.

Lohmann[363] and Schulz and Buchholtz[399] recently wrote on the strength of welded sections of the German copper-chromium steel. Welds were satisfactory, but the data given are of interest with respect to welding methods rather than welding characteristics of the steel.

The properties of a number of copper-chromium steels containing 0.30 per cent carbon were studied by Jones[264] at Woolwich Arsenal. These steels differed from the German steel in that

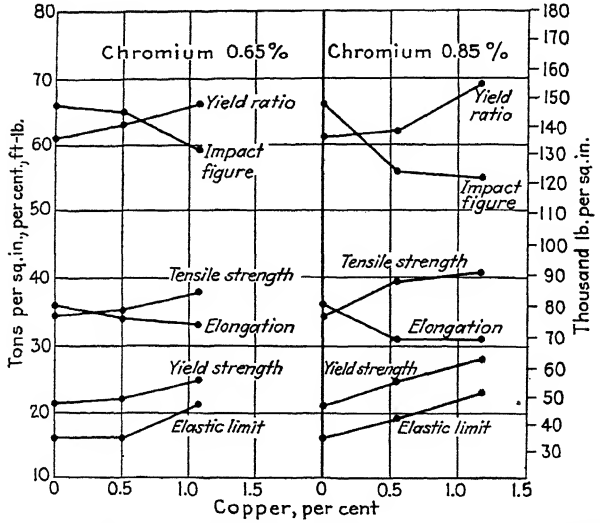


FIG. 171.—Properties of normalized copper-chromium steels containing 0.30 per cent carbon and 0.50 per cent manganese.

the carbon content was a little higher. The steels were in the form of 0.75 × 1.75-in. rolled rods and these rods were normalized at different temperatures. Figure 171 shows the properties of steels containing 0.65 and 0.85 per cent chromium and different percentages of copper. The values indicated are those obtained by normalizing at the "most suitable temperature." The yield strength is the stress that produced a permanent elongation of 0.2 per cent. From the values obtained it was concluded that the addition of from 0.5 to 1.2 per cent copper to steels containing as much as 1 per cent chromium leads to a marked improvement in properties.

A copper-chromium structural steel marketed in England under the name "Chromador" has recently received considerable discussion in the technical press.[347,360,382] This steel, according to Lea,[360] contains 0.3 per cent carbon, from 0.7 to 1.1 per cent manganese, from 0.7 to 1.1 per cent chromium, and from 0.25 to 0.50 per cent copper. The steel is usually used in the as-rolled condition and is said to have a yield strength 50 per cent above that of ordinary hot-rolled mild steel.

One of the steels studied by Lewis[325] contained 0.33 per cent carbon, 0.52 per cent copper, and 0.39 per cent chromium. In the as-rolled condition it had a tensile strength of 81,300 lb. per sq. in. and an elongation of 25 per cent in 8 in.

The Richardsons[102] made atmospheric-corrosion tests on some copper-chromium steels which indicated that copper was just as effective in increasing resistance to atmospheric attack in steels containing up to 1.5 per cent chromium as it is in unalloyed steels. It should be mentioned, however, that the exposure time (8 months) was so short as to render the results of questionable value.

In the 1934 Howe Memorial Lecture* Speller said:

> In the atmosphere the addition of 0.25 per cent copper will usually double or treble the life of steel and the addition of 1 per cent chromium with copper will about double the life again and at the same time add nearly 50 per cent to the strength of the steel, so that in this case the weight and thickness may be materially reduced for certain purposes. Low-alloy steels of this type are finding a wide field of use for roofing, parts of railway cars, and other exposed structures.

A corrosion-resistant steel, described as a copper-chromium-silicon steel, was recently advertised by the United States Steel Corporation. According to a private communication from John Johnston of the corporation's research laboratory, the steel has the following composition and properties:

Element	Percentage
Carbon, maximum	0.10
Manganese	0.10 to 0.30
Phosphorus	0.10 to 0.20
Sulphur, maximum	0.05
Silicon	0.50 to 1.00
Copper	0.30 to 0.50
Chromium	0.50 to 1.50

* To be published in *Transactions* of the American Institute of Mining and Metallurgical Engineers.

Properties	
Tensile strength, lb. per sq. in.	65,000 to 75,000
Yield strength, lb. per sq. in.	50,000 to 60,000
Elongation in 2 in., per cent	25
Izod impact resistance, ft-lb	60
Endurance limit, lb. per sq. in.	45,000
Weldability	Good
Resistance to atmospheric corrosion	4 to 6 times that of ordinary steel

Izod tests show that it remains ductile at low temperatures at which many ordinary steels become brittle.

In determining the thermal expansion of various steels over a wide range of temperatures Souder and Hidnert[121] used two copper-chromium steels; the temperature-length curves of these steels were quite similar to curves for carbon and other low-alloy steels.

Satoh[269] found that the surface Brinell hardness of a steel containing approximately 0.1 per cent carbon, 1 per cent chromium, and 0.6 per cent copper increased from 144 to 547 on nitriding, but that the surface hardness of a steel differing only in that it contained 1.2 per cent copper did not change on nitriding.

159. Nickel-chromium-copper Steels.—Compositions of four steels used by Oertel and Leveringhaus[137] in studying the influence of copper in nickel-chromium steels are listed in Table 97.

TABLE 97.—ANALYSES OF STEELS MADE BY OERTEL AND LEVERINGHAUS[137]

Number	Composition, per cent							
	C	Mn	Si	P	S	Cr	Ni	Cu
1	0.43	0.38	0.52	0.014	0.020	1.04	4.40	0.19
2	0.43	0.37	0.56	0.013	0.030	1.03	4.46	0.78
3	0.41	0.35	0.49	0.012	0.024	1.02	4.44	1.15
4	0.40	0.38	0.54	0.015	0.026	1.05	4.48	2.20

They were melted in a crucible, cast into ingots weighing 40 kg. (88 lb.), and forged to either 25-mm. (0.98-in.) rounds or rectangular sections 17 × 32 mm. (0.67 × 1.26 in.). No difficulties were encountered in forging. The properties of the steels after having received different heat treatments are given in Table 98. As the copper content increased from 0.19 to 2.20 per cent, values of tensile and yield strength increased slightly, but values

TABLE 98.—PROPERTIES OF NICKEL-CHROMIUM-COPPER STEELS*

Number	Copper, per cent	Heat treatment	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation, $l=5.65\sqrt{A}$, per cent	Reduction of area, per cent	Brinell hardness	Charpy impact, m-kg. per sq. cm.
1	0.19	Annealed at 550°C. (1020°F.)	125,700	95,700	21.9	53.8	262	17.7
2	0.78		135,500	107,500	20.6	52.8	269	13.4
3	1.15		128,500	96,000	22.5	54.4	269	15.7
4	2.20		139,100	101,100	16.4	46.5	277	13.1
1	0.19	Oil quenched from 800°C. (1470°F.) and tempered for 30 min. at 400°C. (750°F.)	213,300	.....	9.2	29.4	415	7.15
2	0.78		222,000	.....	7.0	19.0	429	6.90
3	1.15		216,400	.....	8.0	24.3	429	5.00
4	2.20		228,300	.....	8.0	11.65	444	2.31
1	0.19	Quenched as above and tempered for 30 min. at 500°C. (930°F.)	186,500	172,800	11.4	42.0	363	10.9
2	0.78		197,500	177,500	10.6	37.4	388	10.1
3	1.15		193,500	176,400	12.3	34.2	388	7.2
4	2.20		201,600	182,300	11.0	24.1	415	6.8
1	0.19	Quenched as above and tempered for 30 min. at 600°C. (1110°F.)	152,400	129,500	16.8	55.1	302	18.5
2	0.78		158,900	136,600	14.4	50.6	321	15.5
3	1.15		159,700	139,500	16.1	49.0	321	14.8
4	2.20		163,300	147,000	14.8	46.2	321	12.8

* Oertel and Leveringhaus.[137]

of elongation, reduction of area, and notched-bar impact resistance decreased. The tempered samples used in obtaining the data given in Table 98 were quenched in oil from the tempering temperature. In order to determine whether or not the copper

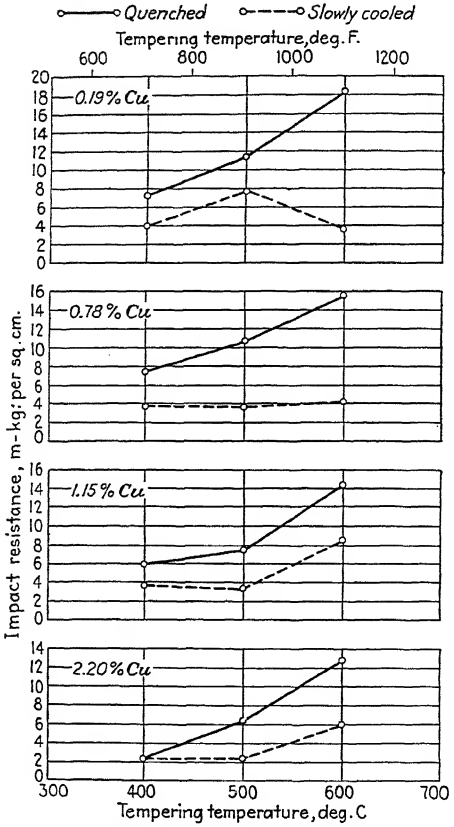


FIG. 172.—Charpy impact resistance of nickel-chromium-copper steels quenched in oil from 800°C. (1470°F.) and tempered as indicated. (*Oertel and Leverinnhaus*.[137])

influenced susceptibility to temper brittleness, additional samples were tempered, for 1-hr. periods, and cooled slowly from the tempering temperature. Values obtained on samples cooled by the two different methods are plotted in Fig. 172, which indicates that all four steels were susceptible to temper brittleness and that susceptibility was not affected by variation in copper content.

From the results of their study Oertel and Leveringhaus concluded that small amounts of copper inadvertently introduced into nickel-chromium steels would not be harmful, but that the properties were not improved by the addition of copper.

A few data were cited by Grenet[82] to prove that the addition of copper to chromium or nickel-chromium steels increased the penetration of the hardening effect, but his data do not offer very satisfactory proof of this inference. The depth-hardening ability was judged by the surface hardness of bars cooled in still air, in some cases several bars being wired together.

The Japanese investigator Hayashi[203] made tensile tests at various temperatures on a series of nickel-chromium steels containing from 0.04 to 3.05 per cent copper and found that the copper had no measurable influence on the properties of the steels at room temperature. At high temperatures elongation decreased as the copper content increased.

Cooling curves for a steel containing 0.39 per cent carbon, 2.44 per cent nickel, 1.83 per cent chromium, and 1.73 per cent copper were shown by Dejean.[91] As the temperature from which the samples were cooled was raised, the Ar_1 point was lowered to become the Ar'' point. The curves give no clue regarding the influence of copper in the steel used.

160. Copper-molybdenum Steels.—As mentioned on page 434 of "The Alloys of Iron and Molybdenum," an open-hearth iron marketed under the trade name "Toncan" contains a minimum copper content of 0.40 per cent and a minimum molybdenum content of 0.05 per cent. The alloy is, therefore, a low-carbon copper-bearing steel containing a trace of molybdenum. Reliable data indicating just how the properties of this material differ from those of copper-bearing steel containing no molybdenum are not available. Among the articles dealing with the alloy under discussion, those by Tupholme,[193] Romer and Eaton,[213] Miller,[299] as well as an anonymous article[310] may be mentioned.

The American Society for Testing Materials' tentative specification (*A*-129-30*T*) for "open-hearth iron plates of flange quality" allows three types of chemical composition, one corresponding to ingot iron without added copper, one to copper-bearing iron with a minimum of 0.20 per cent copper, and the other to iron with a minimum of 0.40 per cent copper and 0.05 per cent molybdenum. The physical requirements of 44,000 lb. per sq. in. tensile strength, 27,500 lb. per sq. in. yield strength, 25 per cent

elongation in 8 in. (with usual modifications in elongation for variation in thickness), as well as those of the bend-test results are not varied as each of the three compositions is supposed to conform to the minimum requirements.

For use at moderately high temperatures, such as in fire-box plate, the makers of Toncan raise the copper to 0.75 per cent.

Some of the properties of a steel containing 0.03 per cent carbon, 0.45 per cent copper, and 0.1 per cent molybdenum were reported by Lewis.[325] This steel as normalized had a Brinell hardness of 107. Quenching increased the Brinell hardness to 170. The following hardness values were observed after tempering at the temperatures shown, which may indicate that the steel was amenable in a slight degree to precipitation hardening:

Tempering temperature		Brinell hardness
°C.	°F.	
300	570	121
400	750	121
500	930	116
550	1020	121
600	1110	126
650	1200	149

According to Nehl,[329] low-carbon steel containing approximately 0.20 per cent copper and 0.30 per cent molybdenum is used in boiler construction. The function of the copper is evidently to increase the resistance to corrosion and that of molybdenum to improve the high-temperature properties.

The high-temperature properties of a steel containing 0.13 per cent carbon, 0.19 per cent copper, and 0.25 per cent molybdenum were investigated by Pomp and Enders.[331] At a temperature of 600°C. (1110°F.) this steel had a higher so-called creep limit than carbon steel, but this was undoubtedly due primarily to the molybdenum content rather than the copper content.

It is understood that a high-copper steel containing molybdenum and suitable for the fabrication of high-strength normalized sheet will soon be announced.*

Among the steels used by Bailey and Roberts[311] in studying deterioration at elevated temperatures was one containing 0.125

*See article by H. L. Miller, *Metals & Alloys*, v. 5, 1934, pp. 227–228, which appeared while this book was in press.

per cent carbon, 0.53 per cent manganese, 0.5 per cent nickel, 0.4 per cent molybdenum, and 0.47 per cent copper. This steel was normalized from 900°C. (1650°F.), after which it had a Brinell hardness of 132 and an impact resistance of 49 to 55 ft-lb. After being subjected to a temperature of 450°C. (840°F.) for 200 hr. while under a tensile stress of 11,200 lb. per sq. in., its impact resistance was only 16 to 17 ft-lb. From these data it was concluded that copper in small amounts (0.5 per cent) made the steel susceptible to embrittlement, though the data do not prove that copper was responsible for the deterioration.

One of the steels used by Coffman[315] in his study of nitriding contained 0.07 per cent carbon, 0.62 per cent copper, and 0.79 per cent molybdenum. This steel did not yield a particularly hard case when nitrided; the maximum Vickers-Brinell hardness of the case was 543 as compared with 857 for the case of an aluminum-molybdenum steel.

TABLE 99.—COMPOSITION AND PROPERTIES OF 19 CAST LOW-ALLOY STEELS CONTAINING COPPER*

Content	Composition, per cent									
	C		Mn		Si		Ni		Cu	
Minimum.	0.27	0.030	0.79		31	0.033	1.10		0.21	
Maximum	0.36	0.042	1.21		42	0.049	1.80		0.85	
Average..	0.33	0.034	1.05		36	0.042	1.43		0.63	

Properties	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent
Minimum.	81,300	53,500	21	31
Maximum.	96,100	59,100	25	44
Average...	91,000	55,900	23.0	37.0

* Rhodes.[79]
† Reported as proportional limit.

161. Miscellaneous Steels.—A low-cost steel suitable for either castings or forgings, according to Rhodes,[79] contains 0.30 to 0.35 per cent carbon, 1 to 1.20 per cent manganese, 1.5 to 1.8 per cent nickel, and 0.5 to 0.8 per cent copper. Properties of castings made from steels of this type are given in Table 99,

which shows average, minimum, and maximum values obtained from tests made on samples from 19 heats. Transverse properties of forged samples from the same steels are given in Table 100. Longitudinal properties as judged by two samples were:

Properties	Sample 1	Sample 2
Tensile strength, lb. per sq. in	105,400	95,100
Yield strength, lb. per sq. in	72,300	67,200
Elongation in 2 in., per cent	24.8	28.7
Reduction of area, per cent	56.4	65.7

TABLE 100.—TRANSVERSE PROPERTIES OF 11 FORGED STEELS OF THE COMPOSITIONS GIVEN IN TABLE 99*

Properties	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent
Minimum.	98,900	63,300	17.35	30.8
Maximum.	119,800	89,900	26.45	52.4
Average...	106,300	73,250	22.2	44.9

* Rhodes.[79]
† Reported as proportional limit.

The addition of 0.50 per cent chromium to the manganese-nickel-copper steel was alleged to improve the alloy to such an extent that its properties were equal to those of a 3 per cent nickel, 1 per cent chromium steel. Longitudinal properties of one sample and average transverse properties of seven samples of forgings from such a steel (not heat treated?) were:

Direction	Tensile strength, lb. per sq. in.	Yield strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent
Longitudinal.	130,400	117,600	19.0	47.6
Transverse...	139,900	110,000	16.5	42.9

Several of the 193 heats of steel tested by Burgess and Woodward[112] in a study of armor plate contained copper in addition to other alloying elements. The analyses of the copper-containing steels were:

Number	Composition, per cent					
	C	Si	Mn	Ni	Zr	Cu
1285	0.35	1.40	0.76	2.55	0.70	0.62
1282	0.45	1.10	0.84	1.90	....	1.35
1286	0.46	1.30	0.82	2.55	....	0.64
1280	0.49	1.25	1.03	2.45	....	0.55
1283	0.50	1.25	0.78	2.60	....	0.36
1281	0.51	1.35	1.04	2.90	....	0.62
1279	0.58	0.23	0.90	2.45	....	0.62

These steels were rolled into plates and tested as normalized and after quenching in oil and tempering at 175°C. (345°F.). It was concluded that "in those steels in which the sum of the nickel and copper, together with the silicon and carbon, are in a favorable ratio the usual high tensile strengths are secured, but with a reduction of the ductility and toughness."

Fatigue data on many steels secured by Houdremont and Mailänder[234] indicated that a manganese-copper structural steel in the as-rolled condition had a high endurance ratio (0.60).

TABLE 101.—COMPOSITION OF STEELS MADE BY RUHNKE[334]

Number	Composition, per cent					
	C	Mn	Si	S	Cu	Mo
1	0.21	1.10	0.65	0.028		
3	0.15	0.28	0.30	0.049	0.80	
4	0.15	0.64	0.69	0.042	1.61	
5	0.15	1.26	1.61	0.037	1.47	
6	0.15	1.04	1.13	0.033	2.58	
7	0.56	1.46	1.24	0.019	1.49	0.41
8	0.59	2.07	1.61	.....	3.58	1.10
9	0.40	1.28	1.35	.....	3.68	0.83

The analyses of some copper steels prepared by Ruhnke[334] are given in Table 101. These steels were made in a small arc furnace and cast into ingots 12 in. long, 2.5 in. square at the base, and 3 in. square at the top. Alloys 8 and 9 could not be forged. The other steels were forged into 0.75-in. square bars. Steels 1 to 6, inclusive, forged as readily as the average medium forging steel, but a checked surface was found on steels 3, 4, 5,

and 6, which became more pronounced as the copper content of the steels increased. Steel 7 did not forge so readily as the other forgeable steels, and after cooling a thin film of copper could be seen on the surface.

TABLE 102.—PROPERTIES OF STEELS DESCRIBED IN TABLE 101*

Steel number	Quenched or normalized	Tempered °F.	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Rockwell *B* hardness	Rockwell *C* hardness
	Quenched	540 1000	105,500	85,500		61.1	101	
	Quenched	595 1100	99,000	76,600	24.1	65.9	101	
	Quenched	650 1200	85,300	60,400	28.8	70.7	96	
	Normalized		73,700	45,300	37.9	71.0	94	
	Normalized	510 950	73,500	46,100	35.1	69.0	94	
	Quenched	1000	72,250	50,000	34.4	68.5	95	
	Quenched	1100	72,500	48,300	....	69.0	94	
	Quenched	1200	67,700	45,700	33.8	71.2	93	
	Normalized		62,600	40,400	37.6	67.3	93	
	Normalized	510 950	70,000	45,700	33.0	63.9	95	
	Normalized		83,300	61,500	28.2	55.6	99	
	Normalized	510 950	91,100	73,300	25.2	54.0	103	
	Quenched	540 1000	133,700	95,000	16.4	42.7		31
	Quenched	595 1100	112,200	76,800	20.5	49.8		26
	Quenched	650 1200	104,800	71,500	24.4	60.9		24
	Normalized		106,100	54,300	26.4	53.0		25
	Normalized	510 950	113,250	80,000	22.1	51.1		27
	Quenched	540 1000	134,250	130,000	18.0	47.4		34
	Quenched	595 1100	129,300	112,800	21.8	55.5		32
	Quenched	650 1200	118,600	106,100	21.8	58.7		28
	Normalized		111,200	71,300	26.1	57.5		27
	Normalized	510 950	111,000	90,000	23.8	55.6		27
	Quenched	540 1000	126,400	65,500	18.4	39.7		30
	Quenched	595 1100	121,800	65,500	21.2	43.4		29
	Quenched	650 1200	121,300	75,500	20.6	46.3		29
	Normalized		154,500	70,000	5.2	10.7		37
	Normalized	510 950	118,000	64,900	23.9	48.9		26

* Ruhnke.(334)

† Reported as proportional limit.

Properties of quenched and tempered, normalized, and normalized and tempered samples of the steels whose compositions are given in Table 101 are given in Table 102. The low-carbon steels were quenched in water from 920°C. (1690°F.); the high-carbon steels were quenched in water from 795°C.

(1465°F.). The normalizing temperature was 940°C. (1725°F.) for the low-carbon steels and 820°C. (1510°F.) for the high-carbon steels. A 1-hr. tempering period was used. The hardness of all of the quenched steels decreased as the tempering temperature was raised, indicating that the softening due to tempering overbalanced any hardening due to precipitation of copper. The hardness of the normalized samples of steels 3, 4, and 5 increased slightly on tempering, which may be attributed to precipitation of copper. Precipitation-hardening phenomena for the other steels are not indicated by the data in Table 102. Samples of the steels after having been given different heat treatments were held for a period of 8 weeks at 150°C. (300°F.) and the changes in hardness observed. Most of the steels showed a slight increase in hardness, which was attributed to the precipitation of copper at this low temperature. The authors of this monograph believe that such a conclusion is unwarranted, for the increase in hardness values was small and uncertain, and, if real, it may have resulted from precipitation of interstitial elements known to be able to harden iron alloys by precipitation at a low temperature.

Properties of two chromium-vanadium-copper steels given by de Sveshnikoff[380] are shown below. The steels had been quenched in water from 900°C. (1650°F.).

Composition, per cent					Tempered		Tensile strength, lb. per sq. in.	Yield strength,* lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell hardness
C	Mn	Cr	V	Cu	°C.	°F.					
0.16	0.08	1.14	0.21	1.18	705	1300	108,100	98,400	22.5	63.5	235
0.32	0.28	0.80	0.28	2.76	605	1125	107,450	70,000	24.0	66.0	241

* Reported as proportional limit.

These steels were used in machine-gun barrels, and their properties were not discussed.

Some cast steels made at the Norfolk Navy Yard and mentioned in a paper by Gillett and Gregg[350] contained as much as 0.89 per cent copper. The steels were not such as to indicate the influence of the copper.

The cast "steel" crankshaft now used in Ford automobiles contains, according to Finney:[391]

Element	Percentage
Carbon	1.25 to 1.40
Manganese	0.50 to 0.60
Silicon	1.90 to 2.10
Chromium	0.35 to 0.40
Copper	2.50 to 2.75
Phosphorus, maximum	0.10
Sulphur, maximum	0.06

While this material is termed "high-carbon, high-copper, chromium-silicon cast steel" in the discussions in technical journals, it contains graphite and its casting properties are evidently those of a high-strength cast or malleable iron rather than steel. While it is alleged that the Patent Office has defined this as a steel, metallurgically it seems to be more properly classified as a high-strength cast iron. It is intermediate among cast steel, cast iron, and malleable iron. According to discussions[385,388] in *Automotive Industries* and *The Foundry*, the material is melted in electric furnaces or duplexed from a cupola to an air furnace using a charge of 40 to 50 per cent steel scrap, the balance being back scrap, pig iron, and the necessary alloying materials. No common gray-iron scrap is used. The metal as cast is white and brittle, resembling malleable iron as cast. The gates and risers weigh nearly as much as the casting.

The castings are put through the following cycle for normalizing, toughening, and strain relief: hold 20 min. at 900°C. (1650°F.); cool to 540°C. (1000°F.) in 1 hr. 30 min.; hold 9 min. at 760°C. (1400°F.), cool to 370°C. (700°F.) in about 2 hr., then air cool. This treatment reduces the average Brinell hardness from an initial value of 350 to one of 300. In the account by Dwyer[388] the cycle is given as: hold at 790°C. (1450°F.) for 1 hr., air cool to 425°C. (800°F.), reheat to 790°C. (1450°F.), air cool rapidly to 425°C. (800°F.), then cool slowly. This treatment is said to give 270 to 300 Brinell.

While machining speeds are reduced over those used with forged crankshafts, the substitution is found to be economical because the crankpin journals are cored and less weight is required in the counterbalances, as only 9 lb. of metal are removed in machining against 24 lb. from the forged shaft. Another reason is because fabrication requires but 54 operations against 62 for the forged shaft. Cold straightening is eliminated as the castings do not warp materially in heat treatment. The finished weight is 56 lb. as compared with 66 lb. for the forged shaft.

It is stated that in a test where the shaft is mounted as in the engine bearings, with the center main bearing set out of alignment so as to produce a total deflection of $\frac{1}{16}$ in., the cast crankshaft will stand up over 2 hr. before fracture, while the forged shaft fails in 1 hr.

It is also claimed[386] that the bearing surfaces of the cast crankshaft give more than twice the mileage of the forged shaft before noticeable wear occurs, although the Brinell hardness is but 300 compared with 444 for the previously used forged shafts.

The surface Brinell hardness values of several copper-containing steels before and after nitriding at 580°C. (1075°F.) for 4.5 hr., according to Satoh,[269] were:

Composition, per cent				Brinell hardness	
C	Cr	Cu	Al	Before nitriding	After nitriding
0.1	1	0.6	..	144	547
0.1	1	1.2	..	163	154
?	..	1.2	2	288	388

As a footnote in a recent book Thum[381] mentioned low-chromium steels containing copper and silicon that have a remarkable resistance to atmospheric corrosion. The favored composition is 1 to 2 per cent chromium, 0.40 to 0.45 per cent copper, and 0.75 to 0.85 per cent silicon. Though not of the stainless type these steels when exposed to the atmosphere have a life two or three times that of ordinary copper-bearing steel, according to Saklatwalla.

C. COPPER IN CORROSION-RESISTANT ALLOYS

Copper has been used in small amounts in both ferritic and austenitic corrosion-resistant iron-chromium or iron-chromium-nickel alloys, although these materials do not as a rule contain copper. Mention also has been made of the use of copper in nickel-silicon corrosion-resistant irons or steels.

162. Copper in Ferritic Corrosion-resistant Alloys Containing Chromium.—According to Monypenny,[300] copper is not generally present in the cutlery type of stainless steels or in rustless irons, but as it has certain definite effects on the corrosion resistance of such alloys its influence on the mechanical properties is of interest. Monypenny shows hardness-versus-tempering-

temperature curves for a steel containing 0.22 per cent carbon, 12.1 per cent chromium, and 1.20 per cent copper and for a steel containing 0.16 per cent carbon, 12.1 per cent chromium, and no copper. These curves indicate that the presence of 1.2 per cent copper lowered the Ac_1 point by about 25°C. (45°F.) and slightly increased the hardness for all tempering temperatures. The effect of the copper was so slight, however, that its presence would not necessitate any modification in the treatment of stainless steels. The steels containing copper "forged and rolled perfectly," and after hardening and tempering they were very tough.

Monypenny concluded that in chromium steels copper has an influence similar to nickel but that even when present in fairly large amounts it does not lead to the production of austenite. Neither of the steels of the following analyses was austenitic when quenched from temperatures up to 1200°C. (2190°F.):

Steel	*A*	*B*
Carbon, per cent....	0.17	0.16
Silicon, per cent....	0.33	0.33
Manganese, per cent	0.11	0.11
Chromium, per cent.	14.0	15.7
Copper, per cent....	5.0	9.85

In an article published in 1924, Saklatwalla[149] claimed that the presence of from 0.5 to 1.5 per cent copper in stainless steels, especially in steels containing less than 0.15 per cent carbon, increases the non-corrosive properties and tends to decrease the oxidation brought about by heating in an oxidizing atmosphere. In order to determine the effectiveness oi copper in stainless steels in increasing the resistance to acids Monypenny[300] tested steels of the following compositions, which had been quenched from 950°C. (1740°F.) and tempered at 700°C. (1290°F.):

Steel		*B*
Carbon, per cent....	0.16	0.22
Silicon, per cent....	0.28	0.28
Manganese, per cent	0.17	0.17
Chromium, per cent.	12.1	12.1
Nickel, per cent.....	0.44	0.47
Copper, per cent....	0.08	1.20

The results of the tests are shown in Table 103. Copper had a noticeable effect in increasing resistance to all acids with the exception of nitric acid, but even the copper steel can hardly be described as an "acid-resisting" material.

TABLE 103.—EFFECT OF COPPER ON THE ACID RESISTANCE OF STAINLESS STEEL*

Acid	Strength, per cent	Duration of attack, hr.	Loss, g. per sq. m. per hr.	
			Steel *A*, 0.08 per cent Cu	Steel *B*, 1.20 per cent Cu
Sulphuric	5	7	22.1	10.5
Sulphuric	35	6	265.0	45.0
Sulphuric	50	6	8.8	6.4
Hydrochloric	Normal	7	5.8	1.8
Nitric	Normal	6	7.1	7.6
Acetic	5	24	0.32	0.16

* Monypenny.[300]

While studying 28 stainless steels Strauss and Talley[150] found that one containing 0.24 per cent carbon, 1.08 per cent copper, and 20.44 per cent chromium had rather unusual properties, in that it had a high impact value after quenching from a high temperature. Inasmuch as a material of a similar composition but without copper was not available, it was not possible to determine whether or not the copper had any pronounced influence on the properties of the steel. The investigators thought it improbable that the copper really modified the properties of the steel. The copper-containing steel showed a comparatively good resistance to the salt-spray test.

From a study of stainless irons of various compositions (carbon less than 0.12 per cent, chromium from 10 to 18 per cent), Mochel[171] found that the addition of 1 per cent copper increased the resistance to salt water or to salt spray and that it did not affect the mechanical properties.

Saklatwalla and Demmler[245] found that the addition of 2 per cent copper to stainless iron containing 14 per cent chromium appreciably increased strength and hardness, as is evident from the following data obtained from annealed steels:

Composition and properties	Steel	
	A	*B*
Carbon, per cent	0.11	0.12
Chromium, per cent	14.25	13.33
Copper, per cent	0.05	1.30
Silicon, per cent	0.26	0.23
Manganese, per cent	0.38	0.49
Nickel, per cent	0.16	0.08
Tensile strength, lb. per sq. in	71,500	98,050
Yield strength, lb. per sq. in.	42,000	74,450
Elongation in 2 in., per cent	40.0	26.5
Reduction of area, per cent	78.0	67.6
Brinell hardness	146	205
Izod impact, ft-lb	93.5	91.0

Alloys containing from 0.05 to 3.30 per cent chromium, and from 0.23 to 0.57 per cent copper, were also studied, but the data obtained do not permit an evaluation of the influence of copper. It was suggested that the low-alloy chromium-copper steels could be cheaply produced and that their corrosion resistance was intermediate between that of ordinary iron or steel and high-chromium iron or steel.

A recent article by DeVries[317] described the properties of a "new rustless iron alloy" containing approximately 16 per cent chromium, 1 per cent silicon, 1 per cent copper, 0.40 per cent manganese, and not over 0.10 per cent carbon.

Of the "stainless" alloys whose corrosion-fatigue properties were reported by McAdam, some contained as much as 0.9 per cent copper, but the data do not indicate whether or not the copper influenced the properties of these steels and irons.

Lounsberry and Breeler[240] found that as much as 1.26 per cent copper had a negligible influence on the hardness and microstructure of steels containing from 0.40 to 0.60 per cent carbon, 8 to 10 per cent chromium, and 4 to 6 per cent aluminum. Copper, however, produced a decided increase in resistance to atmospheric corrosion, as judged from the appearance of samples exposed for 107 days during the winter months.

The life of a number of corrosion-resistant alloys under conditions simulating those met in anthracite-breaker chutes was determined by Keene and McFarland.[354] They found that the

alloy with the longest life contained 0.30 per cent carbon, 20 per cent chromium, and 1 per cent copper.

In the "Book of Stainless Steels"[351] Parker discussed the influence of copper in low-carbon high-chromium alloys. According to him, only about 4 per cent copper can be dissolved in this material, as higher percentages of copper make the alloy red-short. If copper is to be added, an addition of 1 per cent is desirable, for little is to be gained by increasing the copper above this amount. One per cent of copper influences the properties in three ways. First, it produces a more uniform response to heat treatment. Second, it increases the tensile strength and hardness of the material. A quenched alloy containing 0.10 per cent carbon and 12 per cent chromium will have a Brinell hardness ranging from 325 to 385, while an alloy in the same condition containing 1 per cent copper will have a Brinell hardness of 400. Third, copper increases the tempering temperature required to produce a given strength or hardness. Copper does not materially change the corrosion resistance, but it slows down attack of certain reagents. In the book mentioned above, DeVries discussed the properties of ferritic or martensitic corrosion-resistant alloys containing 1 per cent copper and 1 per cent silicon. Jones stated that copper was sometimes added to high-chromium steels used for castings in order to offset the effect of the high-carbon content required to give good castings and to reduce the tendency toward grain growth at temperatures above 760°C. (1400°F.). Johnson claimed that a small amount of copper in low-carbon ferritic alloys materially influenced the annealing operation in that it increased the time necessary to obtain proper softness. Palmer mentioned the use of from 0.20 to 0.40 per cent sulphur in martensitic alloys to increase machinability and said that the sulphur was sometimes supplemented by small amounts of copper.

163. Copper in Austenitic Corrosion-resistant Alloys Containing Chromium.—In studying the susceptibility of alloys of the 18-8 type,* Krivobok and associates[358] used a number of alloys containing both copper (as much as 3.20 per cent) and molybdenum (as much as 3.08 per cent). Some of the copper-molybdenum alloys showed little tendency toward deterioration, but it is not possible to determine whether or not the copper present

* Eighteen per cent chromium, 8 per cent nickel, and carbon as low as possible.

influenced the behavior. A recent study by Rollason,[375] however, indicated that the presence of 2.02 per cent copper in austenitic nickel-chromium steels increased the susceptibility to intergranular attack at ordinary temperature after the steel had been held at elevated temperatures. The copper increased the general resistance to attack by dilute hydrochloric and sulphuric acids and by ammonium chloride.

A note by Robak,[372] in 1933, stated that Tigerschiöld, in Sweden, had found that, by the addition of silicon and copper, austenitic chromium-nickel steels could be made more resistant to attack by sulphuric acid. The alloys should contain from 22 to 35 per cent nickel, as much as 3 per cent chromium, from 4 to 6 per cent silicon, from 0.5 to 2.5 per cent copper, and from 0.05 to 0.2 per cent carbon.

Tindula[338] found that the addition of 1 per cent copper and 1 per cent molybdenum to alloys of the 18-8 type did not prevent embrittlement brought about by heating at certain elevated temperatures.

According to Monypenny,[328] the addition of 2 per cent copper to chromium-nickel steels increases resistance to sulphuric acid but not so much as the addition of molybdenum.

In the "Book of Stainless Steels"[381] Mathews wrote that the addition of copper to alloys of the 18-8 type reduced corrosion by cold and dilute hydrochloric acid, ammonium chloride, and brines. Lee stated that the addition of copper to the alloy increased resistance to acetic acid.

Kuznetzoff and Liferenko[359] found that the rate of attack in 20 per cent sulphuric acid and 4 per cent hydrochloric acid was less for an alloy of the 18-8 type containing 2.6 per cent copper and 2.8 per cent molybdenum than for a similar alloy without copper or molybdenum. An alloy with 1.45 per cent manganese, 1.1 per cent copper, and 1.5 per cent molybdenum also had a high resistance to acid attack. The influence of copper in the absence of molybdenum was not studied but it was found that the addition of copper to an alloy containing 1.5 per cent molybdenum increased the resistance to acid attack.

According to Becket,[255] the addition of 0.5 to 3 per cent copper to austenitic manganese-chromium steels enhances the resistance to corrosive attack. Higher proportions of copper tend to make the material hot-short. In another article, Becket[313] mentioned a steel containing 18 per cent chromium, 6 per cent manga-

nese, 4 per cent nickel, and 1 per cent copper, which was more resistant to a variety of chemical attack than chromium-manganese-copper steel.

In the book[381] mentioned above, Becket and Franks gave the properties of some chromium-manganese-copper steels and gave the following composition as typical for these steels:

Element	Percentage
Carbon, maximum	0.12
Silicon	0.20 to 0.50
Manganese	8.5 to 10
Chromium	17 to 19
Copper	0.75 to 1.10
Nickel, maximum	0.50

164. Copper in Other Corrosion-resistant Alloys.—A corrosion-resistant iron-base alloy mentioned by Leprevost[145] contains 16 per cent silicon and 8 per cent copper. The copper toughens the alloy, but the material is too hard to be machinable. It is resistant to concentrated nitric acid and dilute sulphuric acid but is rapidly dissolved by hydrochloric acid.

A corrosion-resistant alloy mentioned in an anonymous article[221,222] was said to be a nickel-silicon steel containing copper.

The resistance to attack by sulphuric acid of high-nickel alloys containing different amounts of copper was studied by Miller.[326]

165. Copper in Tool Steels.—Copper is never added intentionally to tool steels, and its presence in such materials has been regarded as undesirable, but the limited data available indicate that when present in amounts that might be inadvertently introduced it is not harmful. In determining the influence of small amounts of a number of elements in tool steel, Maurer and Haufe[146] prepared a series of steels containing 1.2 per cent carbon and different amounts of the elements under investigation. One steel contained 0.11 per cent copper, another 0.52 per cent, and a third 1.10 per cent. Rods of these steels were repeatedly quenched from different temperatures until cracks appeared. Copper did not increase the tendency to crack on repeated quenching. Neither did it result in the production of a poor structure as judged by fractures. Specific-gravity determinations of the quenched alloys indicated that copper favored hardening due to quenching as more martensite formed at intermediate quenching temperatures. It was concluded that, contrary to

common opinion, copper has no bad effect on the hardening of carbon tool steel.

In his recent book Brearley[344] spoke of trying to obtain a satisfactory source of iron for the manufacture of crucible steel in a country other than England and wrote as follows:

> The most readily obtainable of these—Demidoff iron—contained 0.2 or 0.3 per cent of copper, and this, according to our fathers and the text books, was hardly less objectionable in tool steel than sulphur or phosphorus. But, having decided to surmount obstacles and not boggle at them, we made our steels, and, on testing them as best we knew how, found them to be not so bad; they were at least good enough to disturb our faith in the belief that small amounts of copper would play the devil if it got into the pot.

In reference to high-speed steel, McKenna,[94] in 1919, claimed that small amounts of copper were very detrimental. In 1928, Sandberg[214] concluded that copper did not harm high-speed steel unless present in excess of 0.02 per cent.

From the results of tool-life tests on high-speed lathe tools containing as much as 1.77 per cent copper, French and Digges[200,232] concluded that copper adversely affected tool performance with shallow cuts. Copper, however, was less deleterious than tin, arsenic, or antimony. With heavy cuts high-speed steels containing 0.36 or 1.77 per cent copper showed slightly better performance than corresponding steels without copper. In the annealed condition the steel containing 1.77 per cent copper could itself be machined only with difficulty. Copper above 0.4 per cent tended to coarsen the grain of the steel. Hot-working properties were adversely affected only when copper was above 0.8 per cent. Copper did not affect the Rockwell hardness.

Mathews* wrote that, in general, he had found the effects of copper in tool steel to be as follows:

1. To slightly lower the Ar_1 point.
2. It seems to cause no sensitiveness in quenching on repeated quenches. The reported quenching tests were made on rings 0.5 in. thick cut from 1.75-in. round bars of steels containing from 0.75 to 0.85 per cent carbon and from 0.30 to 0.70 per cent copper; comparison tests were made on similar rings cut from material essentially free from copper.
3. It tends to increase depth of hardening and to prevent grain growth at higher quenching temperatures, such as from 845 to 870°C. (1550 to 1600°F.).

* Private communication from John A. Mathews of the Crucible Steel Company of America.

In other words, it seems to have a wider hardening range than similar steel free from copper.

4. Copper-bearing tool steels seem to soften more quickly at higher tempering temperatures.

5. Copper has little influence on the microstructure of either the unetched or etched section.

D. AUTHORS' SUMMARY

1. A number of workers have studied carbon-free iron-copper-nickel alloys, and a complete diagram has been proposed by Tasaki. It is believed, however, that additional work is required to establish a satisfactory diagram. Many data on the properties of the alloys are available and have been summarized in the text. In general, it may be said that the alloys do not possess any outstanding properties that indicate their suitability for particular applications.

2. Some work has been done on the iron-copper-manganese alloys but not enough to allow the construction of a satisfactory diagram. Liquidus and solidus temperatures for the quaternary diagram iron-copper-nickel-manganese have been determined. Some information is available on the constitution of iron-copper-manganese-carbon and of iron-copper-silicon-carbon alloys.

3. Low-alloy copper-nickel steels have good properties, but there is some question as to whether or not the copper really influences the properties. It has been claimed that part of the nickel in the common nickel steels can be replaced by copper without affecting the properties, but some investigational work has indicated that this claim must be accepted with caution until substantiated by more data. Further study of copper-nickel steels, in which their properties are compared with those of copper-free steels containing the same amount of nickel, is needed.

4. Low-alloy copper-silicon, copper-chromium, and copper-manganese-silicon steels have been found to have better properties than carbon steels and to be desirable low-cost structural materials. The copper-chromium steels have received considerable study, and there are many indications that their properties are as good as those of more expensive steels. They seem to have an exceptionally high notched-bar impact resistance at subatmospheric temperatures. When the copper is sufficiently high, these steels respond to a precipitation-hardening treat-

ment. Structural steels of this class are now finding some use in Europe where they are generally used in the as-rolled condition.

5. High-strength copper-molybdenum steels are finding commercial uses in this country. These steels are also of interest for service at elevated temperatures.

6. Several tenths of 1 per cent copper in silicon-steel electric sheet do not affect the magnetic properties and possibly increase the resistance to corrosion.

7. Copper when present to the extent of 1 or 2 per cent in corrosion-resistant chromium steels increases the resistance to attack by certain acids and slightly modifies the mechanical properties. Its influence, however, is not great, and few of the corrosion-resistant alloys contain copper.

8. Copper when present in amounts of about 1 per cent is undesirable in high-speed steels, but there is no good evidence to indicate that several tenths of 1 per cent are really detrimental.

CHAPTER XII

COPPER-RICH ALLOYS

Structure—Physical Properties—Mechanical Properties—Authors' Summary

Copper-iron alloys containing much copper and little iron have not been of great interest from the engineering point of view, for iron may be considered as a deleterious impurity in copper, and it can be almost completely extracted in the fire-refining operation used in producing tough-pitch copper.* Iron, however, is likely to be present in deoxidized copper, and the influence of small amounts of iron on the properties of copper may be of decided interest to producers and users of copper, although it is of secondary importance to those interested in iron-rich alloys. The discussion of the effects of iron on the properties of copper, which will be found below, is, therefore, not so comprehensive as would be desirable in a text dealing mainly with copper or copper-rich alloys.

A. STRUCTURE

As may be seen from the iron-copper diagram in Chapter II, the copper-rich alloys consist either of the copper-rich phase containing a small amount of iron or this phase together with an iron-rich phase. The solubility of iron in copper decreases with falling temperature, and particles of the iron-rich phase may be precipitated from the copper-rich phase at low temperatures and as very small particles—even submicroscopic particles.

166. Macrostructure.—Hanson and Ford[143] examined the macrostructure of a series of copper-rich alloys cast as $1\frac{9}{16}$-in. cylindrical rods. In the series examined iron did not appreciably affect the macrostructure, as is sometimes stated. "There is no great variation in the crystal size, which is rather smaller in the casting with low iron content than in that with a high iron content."

* Copper containing small amounts of oxygen, and the grade generally used in making wire and other products that must have the highest possible electric (or thermal) conductivity.

167. Microstructure.—Typical microstructures of copper containing small amounts of iron were shown by Hanson and Ford.[143] In an alloy containing 3.51 per cent iron the iron-rich phase occurred in the form of dendrites. In an alloy containing 2.99 per cent iron that had been heated for several hours at 1000°C. (1830°F.), cooled slowly during 44 hr. to 870°C. (1600°F.), maintained at this temperature for 111 hr., and then quenched in water, large particles of the iron-rich phase that were not in solution at the higher temperature and small particles that had precipitated on slow cooling were observed. In alloys containing 2.44 and 1.46 per cent iron that had been given the same heat treatment only the small particles were visible, thus indicating that the solubility of iron in copper at 1000°C. (1830°F.) was between 2.44 and 3.51 per cent, and that at 870°C. (1600°F.) it was less than 1.46 per cent. Microstructures of other alloys indicated that the solubility of iron in copper at 740°C. (1365°F.) was less than 0.2 per cent, for particles of iron were visible in an alloy containing 0.2 per cent copper after it had been held at this temperature for 41 hr.

B. PHYSICAL PROPERTIES

The influence of iron on the physical properties of copper may result from the actual entrance of iron in the copper lattice or from a mechanical mixture of particles of the iron-rich phase with the copper. The change in solid solubility of iron in copper with the temperature shows that properties of copper containing small amounts of iron may be modified by heat treatment.

168. Electric Conductivity.—The conductivities of copper-rich alloys containing as much as 2.1 per cent iron were determined by Hanson and Ford.[143] Since the study of the effects of small additions of other elements on the properties of copper is of great importance to the copper industry, it might be well to consider the results of their work in some detail. Melts were made from electrolytic copper and Armco iron. The latter material contained 0.012 per cent carbon, 0.017 per cent silicon, 0.017 per cent sulphur, 0.014 per cent phosphorus, and 0.07 per cent manganese. Electric conductivities of samples that had received various heat treatments were determined. The results are shown in Table 104 and in Fig. 173, where conductivities are expressed as percentage of the international standard for annealed copper. For a material with a conductivity of 100 per cent a wire of uni-

TABLE 104.—EFFECT OF IRON ON THE ELECTRIC PROPERTIES OF COPPER*

Composition, per cent		As rolled		Rolled and annealed at 700°C. (1290°F.) for 30 min., air cooled		Rolled, heated at 1000°C. (1830°F.) for 1 hr., quenched in water		After quenching from 1000°C. (1830°F.), heated at 650°C. (1200°F.) for 1 hr., quenched		Reheated at 650°C. (1200°F.) for 100 hr., quenched		Heated at 650°C. (1200°F.) for 100 hr., quenched, tested at 65°C. (150°F.)
Oxygen	Iron	Conductivity, per cent†	Resistivity‡	Conductivity, per cent†	Resistivity‡	Conductivity, per cent†	Resistivity‡	Conductivity, per cent†	Resistivity‡	Conductivity, per cent†	Resistivity‡	Resistivity‡
0.014	0.06	99.7	1.70	101.0	1.72	90.8	1.89	91.2	1.89	93.5	1.84	2.15
0.003	0.2	54.1	3.18	54.1	3.18	53.2	3.23	56.5	3.05	58.4	2.94	3.24
0.004	0.4	38.3	4.22	40.8	4.49	34.5	4.98	69.9	2.46	56.8	3.03	3.32
0.008	0.73	38.6	4.10	42.0	4.45	27.5	6.25	72.1	2.38	57.4	3.00	3.29
0.005	0.96	38.5	4.43	38.9	4.46	26.5	6.49	70.6	2.44			
0.004	1.38	36.3	4.56	37.7	4.74	30.3	5.67	67.4	2.56			
0.007	1.80	39.1	4.56	37.7	4.40	30.1	5.72	65.5	2.63			
0.008	2.09	39.6	4.55	37.9	4.36	30.4	5.66	65.8	2.62			

* Hanson and Ford.[143]

† Based on International Annealed Copper Standard.

‡ Microhms per cu. cm. at 20°C. (70°F.).

form cross-section, 1 m. (3.3 ft.) long and weighing 1 g. has a resistance of 0.15328 ohm at 20°C. (70°F.). Resistivity values, given in the table, are in terms of microhms per cubic centimeter at 20°C. (70°F.).*

Results indicate that the conductivity of copper is rapidly lowered by the addition of iron up to 0.2 per cent; the conductivity of copper containing more than this amount of iron is greatly affected by the heat treatment to which it has been subjected. Hanson and Ford discussed the effect of heat treatment on the conductivity and related it to the constitution of

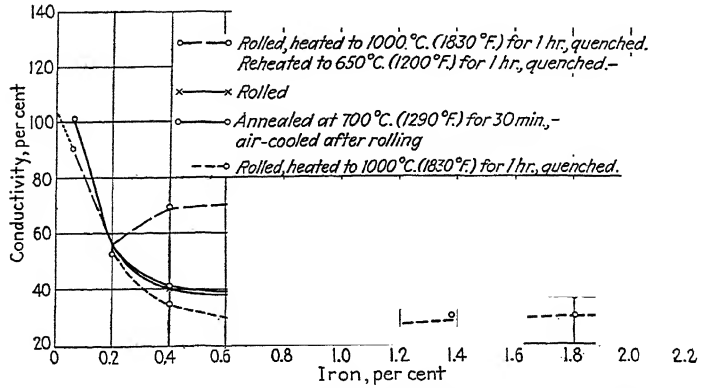


FIG. 173.—Influence of iron on electric conductivity of copper. (*Hanson and*

these alloys. From the curves in Fig. 173 it will be seen that the conductivity of copper falls rapidly, as the iron content increases, and reaches a value of 40 per cent with an iron content of 0.4 per cent. On further increase in iron content it remains practically constant within the limits of the compositions investigated. Annealing at 700°C. (1290°F.) for 30 min. followed by cooling in air had no appreciable effect on the conductivity. When the alloys were reheated to 1000°C. (1830°F.) for 1 hr. and quenched in water, the conductivity was considerably reduced, presumably owing to solution of iron in copper; with an iron concentration of some 0.7 per cent, a conductivity of about 30 per cent was attained and on further increase in iron content remained practically constant. When the quenched alloy was

* It was not stated whether measurements were made on a volume or on a weight basis.

reheated to 650°C. (1200°F.) for 1 hr., the conductivity rose considerably, to 70 per cent of the international standard. This rise in conductivity was presumably due to the precipitation of the iron-rich constituent from the solution.

It will be noted from Fig. 173 that the conductivity of the alloy containing 0.2 per cent iron remains unchanged by reheating at 650°C. (1200°F.); this is thought to be due to the fact that the alloy remains a solid solution supersaturated with iron. Alloys with higher iron content will precipitate the excess iron and this precipitation accounts for the increase in the conductivity of the alloys containing from 0.2 to 0.4 per cent iron. Beyond this percentage of iron the conductivity remains practically constant.

Heuer[184] investigated the effect of very small amounts of iron on the conductivity of copper. He questioned the validity of the results obtained by Hanson and Ford because their samples contained large percentages of oxygen and, therefore, part of the iron in their alloys was present in the form of oxide. Heuer's specimens were prepared as follows: Small castings were forged, machined, thoroughly annealed at 950°C. (1740°F.), the forgings were then drawn cold to 12 gage (0.080 in.) and annealed at 500°C. (930°F.). The conductivity was measured at 20°C. (70°F.). The results given in Table 105 represent the conductivity values corrected for the small amounts of oxygen present in the samples.

169. Magnetic Properties.—As was mentioned in Chapter II, Tammann and Oelsen[272] determined the magnetic susceptibility of a series of copper-rich copper-iron alloys in order to locate the line representing the solid solubility of iron in copper. Sus-

TABLE 105.—EFFECT OF IRON ON ELECTRIC CONDUCTIVITY OF COPPER*

Element, per cent				Conductivity, per cent†
Cu	Fe	O	S	
100.000	0.0002	0.0002	0.0001	102.10
99.995	0.0071	0.0007	0.0006	97.60
99.975	0.0241	0.0007	0.0006	90.05
99.880	0.1212	0.0002	0.0003	64.80
99.778	0.2179	0.0001	0.0001	49.60
99.159	0.8140	0.0003	0.0004	35.60

* Heuer.[184]

† International Annealed Copper Standard.

ceptibility data other than those directly useful in locating the line mentioned were also obtained. In determining magnetic values, samples were placed in a non-homogeneous magnetic field and the force exerted by the field was determined. The force F is given by

$$F = m \cdot S \cdot \frac{\partial H}{\partial y} \qquad \cdot \frac{\partial H}{\partial y}$$

where m is the mass of the sample, S the specific intensity of magnetization, χ the specific susceptibility, H the field strength,

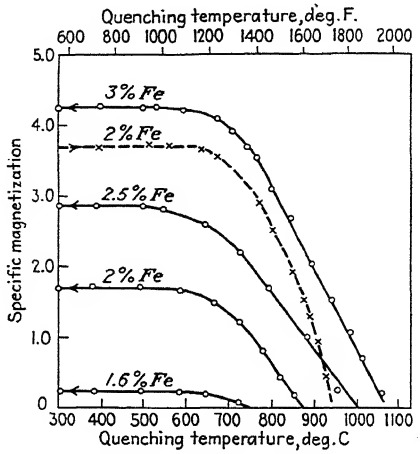


FIG. 174.—Specific magnetization of copper-iron alloys. (*Tammann and*

and $\partial H/\partial y$ the gradient of the field in the y direction. A field strength of 8300 oersteds was used.

Alloys containing only 1.5 per cent iron were not ferromagnetic even when slowly (in 20 hr.) cooled from 1070 to 20°C. (1960 to 70°F.). Alloys with more than 1.5 per cent iron were ferromagnetic after cooling slowly from a high temperature. The solid lines in Fig. 174 show the specific magnetization of several alloys cooled slowly from 1070°C. (1960°F.) to the indicated temperatures, held at these temperatures for 2 hr., and then quenched. As the quenching temperature was lowered ferromagnetism increased, as is to be expected. The dashed line in Fig. 174 shows values for a 2 per cent iron alloy slowly cooled to

room temperature, reheated to different temperatures, and then quenched.

Although alloys containing 1.5 per cent or less iron never became ferromagnetic, their susceptibility was influenced by heat treatment. Curves *A* to *D* of Fig. 175 show susceptibility values for alloys held at the indicated temperatures for 20 min. and then quenched. The susceptibility did not vary regularly with the quenching temperature. Surprisingly, the suscepti-

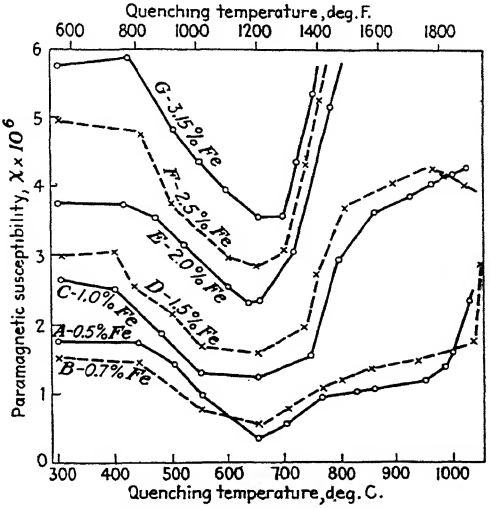


FIG. 175.—Paramagnetic susceptibility of copper-iron alloys. (*Tammann and*

bility seems to depend on whether or not the iron at the quenching temperature was in a ferromagnetic state. Alloys containing from 1.5 to 3 per cent iron were paramagnetic after quenching from 1070°C. (1960°F.), and their susceptibility could be changed by reheating (20 min.) to various temperatures and quenching, as is shown by curves *E*, *F*, and *G* of Fig. 175. A minimum susceptibility for all alloys results on quenching from 650°C. (1200°F.), and the minimum becomes more pronounced as the iron content increases (up to 3 per cent at least).

170. Effect of Cold Work on Magnetic Properties of Copper-rich Alloys.—The specific magnetization of alloys slowly cooled from 1000°C. (1830°F.) can be very greatly increased by cold working (rolling or wire drawing). As may be seen from Fig.

176, alloys containing as little as 0.5 per cent iron became ferromagnetic. Annealed alloys with over 1.5 per cent iron were already ferromagnetic before rolling and reached the maximum susceptibility value at 20 to 30 per cent reduction by cold working. Alloys containing less than 1.5 per cent iron became ferromagnetic and obtained the maximum magnetization after a degree of cold working which was the greater the lower the iron content.

The increase in specific magnetization due to cold work was dependent on the quenching temperature. When the alloys were

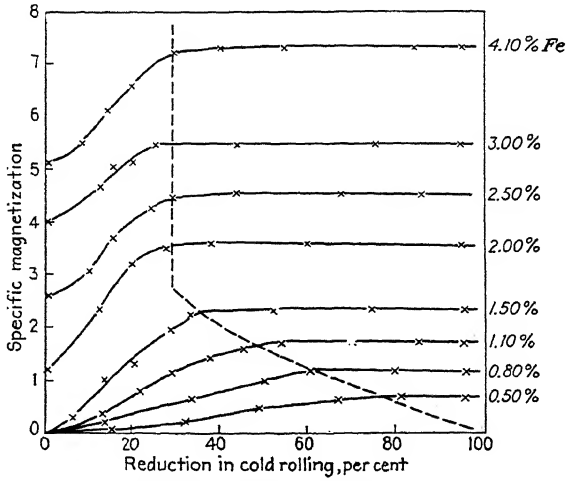


FIG. 176.—Effect of cold working on the specific magnetization of copper-iron alloys. (*Tammann and Oelsen.*[272])

quenched from above 850°C. (1560°F.), cold working caused no increase in specific magnetization; however, when the alloys were quenched from below 850°C. (1560°F.), it did (Fig. 177). Tammann and Oelsen attributed this difference in the magnetic behavior of quenched alloys to the difference in the allotropic state of iron in the precipitated iron-rich constituent. If the iron precipitated in the gamma form, as in specimens quenched from above 850°C. (1560°F.), cold rolling did not influence the magnetizability; in the specimens quenched from below 850°C. (1560°F.) the iron precipitated in the alpha form and the magnetism was strongly increased by cold working. The susceptibility of quenched alloys was found to be dependent on the

duration of heating: it decreased at first, during the first 15 min., and after that increased again.

Results of other investigators (compare Chapter II) have shown that the magnetic susceptibility of annealed copper is increased

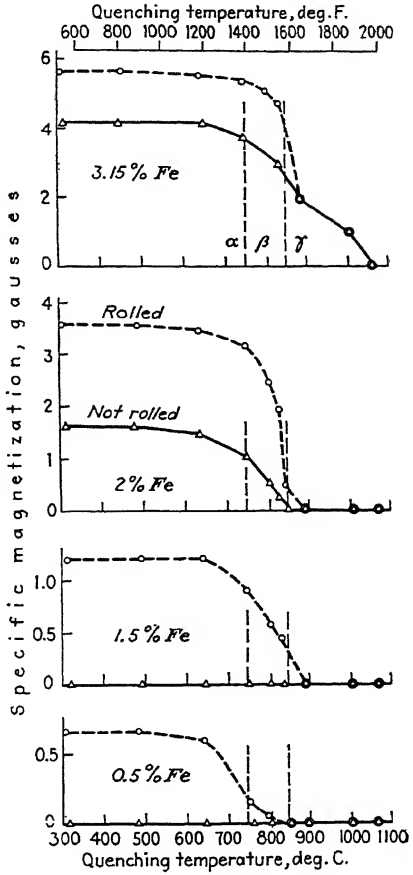


FIG. 177.—Effect of cold work and quenching temperature on the specific magnetization of copper-iron alloys. (*Tammann and Oelsen.*[272])

by cold working and have indicated that this is due to precipitation of iron.

171. Physical Constants.—Some density determinations of copper-rich alloys were made by Hanson and Ford. Their

values were obtained on alloys in the as-cast, as-rolled, and heat-treated conditions and are given in Table 106.

TABLE 106.—DENSITY OF COPPER-RICH ALLOYS*

Composition, per cent		Density (g. per cu. cm.)			
Oxygen	Iron	As cast 1 9/16-in. diameter ingots	As rolled 5/8-in. diameter rods	5/8-in. diameter rods, heated at 700°C. (1290°F.) for 30 min.	As-cast slabs
0.014	0.06	8.3	8.92	8.90	
0.013	0.2	8.82	8.92	8.92	
0.004	0.4	8.71	8.92	8.92	
0.008	0.73	8.63	8.92	8.91	
0.005	0.96	8.72	8.92	8.91	
0.004	1.38	8.73	8.91	8.91	
0.007	1.80	8.74	8.90	8.91	
0.008	2.09	8.70	8.90	8.90	
.....	0.13	....	....	....	8.89
.....	0.30	....	....	....	8.21
.....	0.66	....	....	....	8.91
.....	1.11	....	....	....	8.69
.....	1.83	....	....	....	8.80

* Hanson and Ford.[143]

The variations in the densities are due to unsoundness of the castings; it may be observed that the larger castings are sounder than the smaller chill-cast slabs (last column). The densities of the rolled material, either "as rolled" or after annealing for 30 min. at 700°C. (1290°F.) and cooling in air, are practically constant throughout the series. In all cases, the densities obtained are between 8.90 and 8.92 g. per cu. cm. There is a slight fall in the density as the iron content increases.

C. MECHANICAL PROPERTIES

As is to be expected, the addition of small amounts of iron to copper increases its hardness and strength, but iron is never added to copper for this purpose, and it is intentionally added to but few copper-rich alloys with the exception of the so-called "aluminum-bronzes" and "manganese-bronzes." The iron-copper equilibrium diagram indicates that copper-rich as well as

iron-rich alloys might respond to a precipitation-hardening treatment, and experimentation has shown that the hardness of certain alloys can be increased by such a treatment, but the tensile strength is not greatly increased.

172. Effect of Iron on Malleability and Machinability of Copper.—Iron in small amounts does not appear to impair the malleability of copper. Hanson and Ford[143] cold rolled alloys containing up to 3.5 per cent iron and encountered no trouble in cold rolling billets 1 9/16 in. in diameter to 5/8-in. rounds without annealing. The same billets were also rolled down to 7/8 in. at 800°C. (1470°F.), and then to 5/8-in. rounds after various treatments. In all cases, the material withstood rolling satisfactorily and showed no tendency to crack or split. Heuer[184] experienced no difficulty in cold drawing annealed forged bars 9/16 in. in diameter to 12-gage wire (0.08-in. diameter). The bars contained up to 0.80 per cent iron.

According to Hanson and Ford, copper containing small amounts of iron is rather difficult to machine because the turnings do not easily separate from the metal. The machining of iron-bearing copper is much more difficult than the machining of oxygen-bearing copper, but no more so than any oxygen-free copper as pointed out by Johnson in discussion.

173. Effect of Iron on Tensile Properties of Copper.—Tensile properties of the copper-rich alloys were studied by Hanson and Ford. Their alloys were made from electrolytic copper and Armco iron; the copper was free from arsenic and contained about 0.02 per cent impurities. The alloys were tested (1) as cast, (2) as rolled, and (3) as rolled, annealed 30 min. at 700°C. (1290°F.), and cooled in air. In Table 107 are summarized the results of tests at room temperature and at 250°C. (480°F.).

It may be seen that the tensile strength of the as-rolled material rises very slightly with the iron content. In the case of the annealed material, the effect of iron is considerable, the tensile strength rising from 32,500 lb. per sq. in. in pure copper to 49,500 lb. per sq. in. in the alloy containing 2 per cent iron. The elongation in the as-rolled samples is practically independent of the iron content; in the annealed samples, it drops from 60 per cent in pure copper to 30 per cent in the alloy containing 2 per cent iron. The reduction of area varies very little and is practically identical in the annealed and the as-rolled alloys.

TABLE 107.—TENSILE PROPERTIES OF COPPER-RICH ALLOYS*

Iron, per cent	As cast (chill castings) Tensile strength, lb. per sq. in.	Elongation on $l = 4\sqrt{A}$, per cent	Reduction of area, per cent	As rolled Tensile strength, lb. per sq. in.	Elongation on per cent	Reduction of area, per cent
Chill Castings (Graphite Molds)						
0.06	.....	....	....	51,700	16.3	73
0.2	.....	....	....	49,700	20.4	73
0.4	.....	....	....	52,000	20.4	80
0.73	.....	....	....	48,800	20.4	80
0.96	.....	....	....	51,100	20.0	82
1.38	.....	....	....	51,500	19.6	79
1.80	.....	....	....	54,700	19.3	79
2.09	.....	....	....	56,400	21.3	78
Chill Castings (Cast-iron Slab Molds)						
0.13	24,400	63	74.7			
0.3	26,600	49	44.6			
0.66	27,300	60	82.8			
1.11	30,700	42	66.6			
1.83	31,600	70	53.1			
Rolled						
	Annealed at 700°C. (1290°F.) for 30 min., air cooled			Annealed at 700°C. (1290°F.), tested at 250°C. (480°F.)		
0.06	32,500	57.1	73	23,500	51.7	63
0.2	31,800	60.0	73			
0.4	33,600	59.9	80	23,800	50.8	68
0.73	37,600	51.7	80	25,800	51.4	83
0.96	35,800	45.0	82	27,100	42.5	88
1.38	43,300	29.6	79	32,900	20.0	81
1.8	44,400	29.0	79	36,500	24.6	82
2.09	49,500	33.7	79	38,800	27.1	80

* Hanson and Ford.[143]

The tests at 250°C. (480°F.) showed that the tensile strength of the materials is approximately 9,000 lb. per sq. in. less at 250°C. (480°F.) than at room temperature. The elongation was found

TABLE 108.—EFFECT OF HEAT TREATMENT ON TENSILE STRENGTH OF COPPER-RICH ALLOYS*

Heat treatment	Iron, per cent															
	0.06		0.2		0.4		0.73		0.96		1.38		1.80		2.09	
	T.S.†	Elong.‡	T.S.	Elong.	T.S.	Elong.	T.S.	Elong.	T.S.	Elong.	T.S.	Elong.	T.S.	Elong.	T.S.	Elong.
Quenched from 1000°C. (1830°F.)	24,600 27,100	15.0 10.0	32,000	27.0	32,700	26.0	29,000	28.0	30,700	27.0	34,500	29.0	36,500	28.0	48,200	36.0
Air cooled from 1000°C. (1830°F.)	27,500 23,800	16.5 17.0	31,800	10.7	31,600	27.5	31,800	33.0	34,700	26.5	42,100	36.0	43,500	36.0	46,400	15.9
Furnace cooled from 1000°C (1830°F.)	25,600 28,000	18.0 16.5	30,700	33.0	35,600	26.0	35,000	34.0	36,100	32.0	38,400	33.0	39,200	29.5	41,300	45.0
Quenched from 1000°C. (1830°F.). Tempered at 700°C. (1290°F.)	22,900 20,400	12.0 9.5	32,000	35.0	30,700	30.0	31,200	26.5	35,400	29.0	42,400	37.0	31,000	9.0	46,800	23.0
Quenched from 1000°C. (1830°F.). Tempered at 650°C. (1200°F.)	25,800 24,400	16.0 14.0	32,700	31.0	36,800	28.0	33,900	28.0	39,000	29.0	40,500	30.0	39,400	14.0	42,100	14.0
Quenched from 1000°C. (1830°F.). Tempered at 600°C. (1110°F.)	27,100 20,000	22.0 10.5	33,200	28.5	36,300	28.0	34,100	25.0	35,700	26.0	40,300	23.0	43,000	23.0	46,400	18.0
Quenched from 1000°C. (1830°F.). Tempered at 500°C. (930°F.)	27,500 25,300	18.0 15.0	32,700	25.0	34,700	31.0	31,800	22.0	31,800	26.5	34,700	26.0	39,900	29.5	46,200	31.0
Quenched from 1000°C. (1830°F.). Tempered at 400°C. (750°F.)	25,900 21,300	21.0 9.0	31,100	30.0	36,300	27.0	33,200	34.0	30,500	26.0	35,600	33.0	41,300	17.0	44,400	27.0

* Hanson and Ford.[143]
† Tensile strength, lb. per sq. in.
‡ Elongation in 2 in., per cent.

to be slightly less at the higher temperature, and the reduction of area almost the same at both testing temperatures.

In order to investigate the effect of heat treatment on the tensile properties of copper-rich alloys Hanson and Ford tested a large number of strips which had been subjected to various heat treatments. The strips 0.10 in. thick and 1.5 in. wide were rolled from a ⅞-in. hot-rolled bar. The results of the tests, summarized in Table 108, indicate that the treatments produced some increase in tensile strength, presumably due to the precipitation of the iron-rich constituent in a state of very fine division.

174. Effect of Iron on Hardness of Copper.—The compositions and Brinell hardness numbers of cast alloys (using a load of 500 kg. and a ball 10 mm. in diameter) determined by Hanson and Ford are shown below:

Iron, per cent...	0.06	0.2	0.4	0.73	0.96	1.38	1.8	2.09
Brinell hardness.	28	28.2	35	44	45	45	49.5	49

It may be seen that the hardness rises from 28 in pure copper to 49 in copper containing 2 per cent iron. The hardness increases rapidly as the iron increases from 0 to 0.7 per cent; further additions of iron raise the hardness relatively little.

The effect of heat treatment was also investigated by Hanson and Ford. Two samples of an alloy containing 0.7 per cent iron were heated to 1000°C. (1830°F.) for 7 and 3 hr., after which they were quenched in water, and reheated for 1 hr. at different temperatures. It will be seen from Table 109 that the hardness of the material reached a maximum in the sample reheated to 660°C. (1220°F.). The effect of annealing for 7 hr. at 1000°C. (1830°F.) was not appreciably different from annealing for 3 hr. at this temperature, indicating that most of the iron became dissolved in 3 hr. at 1000°C. (1830°F.).

The effect of heating the quenched alloys for a longer time at temperatures lower than 650°C. (1200°F.) was investigated. Tests were made immediately after quenching and from time to time during the course of reheating, the bars being cooled before the hardness was determined. As may be seen in Fig. 178, reheating to 300°C. (570°F.) had very little effect on the hardness; 400°C. (750°F.) produced an appreciable hardening after 10 days. Reheating for 3 days at 500°C. (930°F.) increased the

hardness from 35 to 49; on further time the hardness increased slightly and then reached a constant value of 54. This maximum hardness is practically the same as that obtained by a short reheating (1 hr.) at 660°C. (1220°F.).

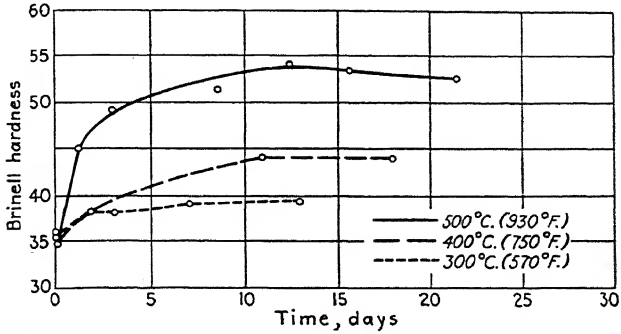


FIG. 178.—Precipitation hardening of a high-copper alloy (0.7 per cent iron), quenched from 1000°C. (1830°F.). (*Hanson and Ford.*[143])

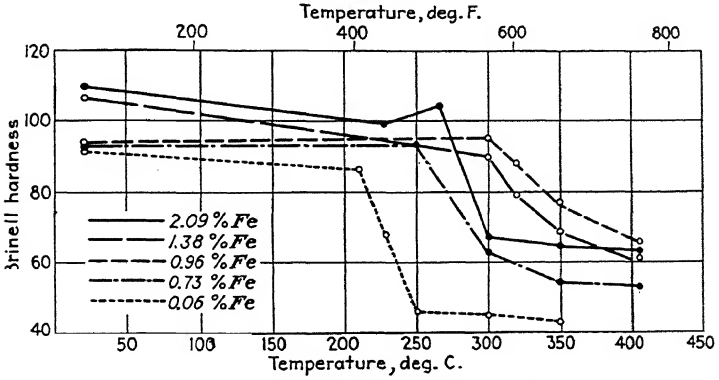


FIG. 179.—Effect of iron on softening temperature of copper. Heated for 15 min. at each temperature. (*Hanson and Ford.*[143])

On holding at room temperature, no appreciable hardening could be detected.

175. Recrystallization Temperatures.—It has been shown by Hanson and Ford that small amounts of iron considerably raise the softening temperature of cold-worked copper. As may be seen from Fig. 179, cold-worked copper containing 0.6 per cent iron begins to soften at 210°C. (410°F.) when heated for 15 min., and copper containing 1.38 per cent iron begins to soften at

300°C. (570°F.). Strips 0.1 in. thick that had been cold rolled from rods $\frac{7}{8}$ in. in diameter were used in the tests.

TABLE 109.—EFFECT OF HEAT TREATMENT ON HARDNESS OF COPPER-RICH ALLOYS (0.7 PER CENT IRON)*

Treatment	Reheating temperature†		Brinell hardness
	°C.	°F.	
Heated 7 hr. at 1000°C. (1830°F.), quenched in water and reheated.	570	1060	42.5
	600	1110	47
	630	1165	49
	650	1200	51
	675	1245	51
	700	1290	46.5
	750	1380	44
Heated 3 hr. at 1000°C. (1830°F.), quenched in water and reheated	570	1060	44
	600	1110	44
	630	1165	48
	650	1200	50
	700	1290	50.5
	750	1380	43

* Hanson and Ford.[143]
† For 1 hr.

176. Relation between Hardness and Magnetic Properties.—Tammann and Oelsen[272] studied the effect of heat treatment on hardness of copper-rich alloys. In Fig. 180 are given their results together with the hardness curve obtained by Hanson and Ford. The curves show close relationships between hardness and magnetization of heat-treated alloys, which are influenced by the same phenomenon, precipitation of the iron-rich constituent. It was found that the maximum hardness (curve B) and the minimum magnetic susceptibility (curves χ) are obtained at the same tempering temperature, and that the electric resistance (curve W) shows a rapid change in this region. It was found further that, after quenching from 1070°C. (1960°F.), the alloys containing up to 3 per cent iron are paramagnetic and their hardness increases with increasing iron content. Curve A of Fig. 181 gives the diameters of impressions produced by a 3-mm. ball and a 15-kg. load. Line C of Fig. 181 gives diameters of impressions for slowly cooled alloys. By slow cooling, alloys with over 1.5 per cent iron were made ferromagnetic and softened,

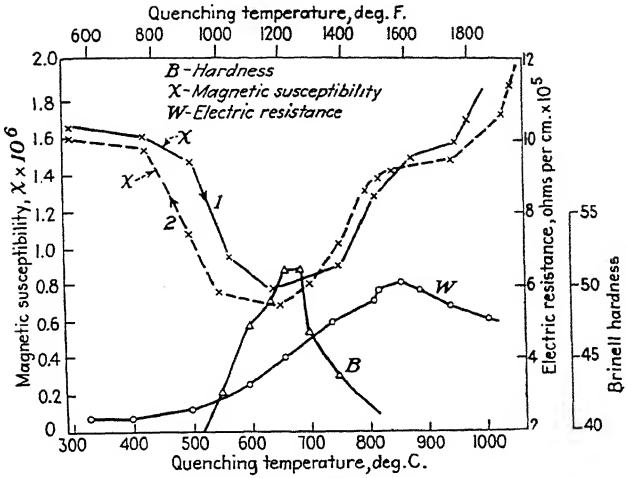


FIG. 180.—Effect of quenching on magnetic susceptibility, electric resistance, and hardness of copper-iron alloys containing 0.7 per cent iron. (*Tammann and*) and *Hanson and Ford* (143))

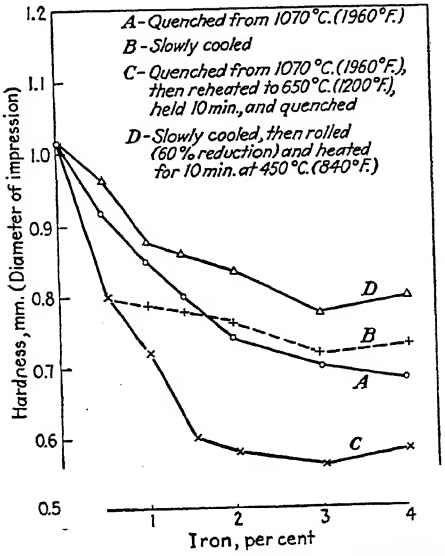


FIG. 181.—Effect of iron on hardness of copper. (*Tammann and*

while the alloys with less than 1.5 per cent iron remained paramagnetic and became harder. Alloys quenched from 1070°C. (1960°F.), then heated at 650°C. (1200°F.) and quenched, became less paramagnetic and their hardness rose considerably, as may be seen by comparing curves *C* and *A* in Fig. 181. Slowly cooled alloys, rolled and heated at 450°C. (840°F.) to remove work hardening, became ferromagnetic and their hardness decreased. The ball impressions are plotted in curve *D* (Fig. 181).

It was also shown by Tammann and Oelsen that the duration of tempering influences the hardness and magnetic susceptibility

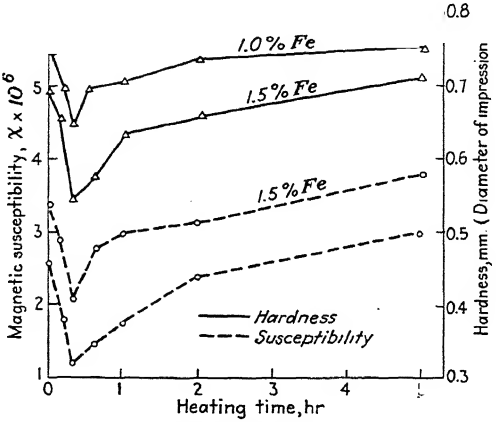


FIG. 182.—Effect of time of reheating to 700°C. (1290°F.) on magnetic susceptibility and hardness of copper-rich alloys. (*Tammann and Oelsen.*[272])

of quenched alloys in the same way as does the raising of reheating temperatures. In Fig. 182, diameters of ball impressions and susceptibility are plotted against the duration of reheating in hours (at 700°C. or 1290°F.) for alloys with 1 and 1.5 per cent iron. The hardness at first increased, and the susceptibility decreased. After about 15 min., the relation was reversed.

From the results obtained by Hanson and Ford, it may be seen that the Brinell hardness of an alloy containing 0.7 per cent iron, quenched from 1000°C. (1830°F.), tempered at 650°C. (1200°F.), and quenched, rose from 35 to 55 Brinell, about 55 per cent (Table 109). However, the tensile strength after similar treatment rose only from 29,000 to 34,000 lb. per sq. in., about 15 per cent.

It may be of interest to note that tempering alloys quenched from 1000°C. (1830°F.) resulted in every case in some improvement in mechanical properties. Hanson and Ford attributed this to the precipitation of iron-rich constituent in a finely divided state. In this respect the iron-copper alloys resemble certain aluminum alloys containing magnesium, silicon, and copper. However, unlike the aluminum alloys, the tensile strength of iron-copper alloys failed to improve in the same ratio as the hardness. Hanson and Ford suggested that the relatively small effect of the precipitated iron-rich constituent on the strength is possibly due to the fact that this constituent is essentially metallic iron containing some dissolved copper and does not itself possess the strength and hardness of intermetallic compounds, which usually have a greater effect on the mechanical properties. This is not necessarily sound reasoning, however, for copper precipitated in iron certainly increases strength.

177. Impact Properties of High-copper Alloys.—The impact properties of high-copper alloys were studied by Hanson and Ford. They carried out a series of Izod impact tests on samples in the as-rolled and the annealed conditions. The compositions and the results are shown in Table 110.

TABLE 110.—EFFECT OF IRON ON IZOD IMPACT PROPERTIES OF COPPER*

Iron, per cent	Energy absorbed, ft-lb.†	
	As rolled	Annealed at 700°C. (1290°F.) for 30 min.
0.06	36	44
0.2	48	43
0.4	64	43
0.73	56.2	51.1
0.96	70.8	62.9
1.38	63.2	58.5
1.80	63.5	65.0
2.09	72.3	70.1

* Hanson and Ford.[143]

† In no case did the specimen fracture.

The results are rather irregular, because the specimens bent over without fracturing.

178. Fatigue Resistance.—The effect of iron on the fatigue range of copper was another of Hanson and Ford's investigations.

They concluded that the fatigue limit increases from ±13,450 lb. per sq. in. in pure copper to ±20,200 lb. per sq. in. in copper containing 2 per cent iron. The tests were made by means of a short-cut method, which has subsequently been proved to be unreliable.

D. AUTHORS' SUMMARY

1. When sufficient iron is present to form an iron-rich phase, this phase is evident in the microstructure as small rounded particles or, when the iron content exceeds 3 per cent, as larger particles that look like dendrites. Small amounts of iron have little influence on the macrostructure of copper.

2. Small amounts of iron do not impair the malleability of copper. Copper containing as much as 3 per cent iron can be worked either hot or cold.

3. The electric conductivity of copper is lowered rapidly by the addition of iron up to 0.2 per cent; further increase in iron content decreases the conductivity less rapidly. The conductivity of copper containing more than 0.2 per cent iron is affected considerably by heat treatment. A precipitation treatment increases, and a solution treatment decreases, the conductivity.

4. The specific intensity of magnetization of copper-rich alloys increases with increase in iron content. The magnetic properties are greatly affected by heat treatment.

5. The tensile strength of copper-rich alloys, up to 2 per cent iron, in the hot-rolled condition rises slightly with the iron content, the ductility being almost independent of iron content. Iron appreciably increases the strength of annealed copper, from 32,500 lb. per sq. in. for pure copper to 50,000 lb. per sq. in. for an alloy containing 2 per cent iron; the elongation being 60 per cent for the pure copper and only 30 per cent for the alloy.

6. In a series of alloys the Brinell hardness rose from 28 to 49 as the copper content rose from nil to 2 per cent. The hardness of certain alloys can be increased by a precipitation-hardening treatment, but the tensile strength cannot be increased correspondingly.

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